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Some Effects of Nuclear Irradiations on Cotton Yarn

Edward S. Gilfillan and Leo Linden

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EARLIER experiments, "Effects of Nuclear Radiations on the Strength of Yarns," [1] on the exposure of certain textile fibers to nuclear radiations, posed the question as to how much the results obtained on cotton might have been affected by the presence of moisture and/or atmospheric oxygen during the irradiation. It is well-known that both beta and gamma radiations produce hydrogen peroxide from moisture and produce ozone from atmospheric oxygen. Both of these powerful oxidizing agents have adverse effects on the physical properties of cellulose. In the original experiments the irradiations were conducted in the facilities of the Brookhaven National Laboratory. No attempt was made to remove any moisture and atmospheric oxygen from the samples preliminary to irradiation; thus it seemed possible that if nuclear radiation had actually brought about an improvement in the physical properties of the cotton irradiated, any benefits might have been masked by the adverse effects from the oxidants that were simultaneously produced. It was therefore decided to investigate the effects of irradiation on cotton in the absence of moisture and atmospheric oxygen. Strength was the property selected as the best index of success.

In the first series of tests irradiated at the Brookhaven National Laboratory, one set of cotton yarns was exposed in a gamma field produced by a cobalt 60 source in which the gamma ray energy was estimated at 1.3 m.e.v. The second set was irradiated in the water-cooled section of the pile and received a dose of about 2.3×10^{17} neutrons per square centimeter, and of these neutrons, 5 out of every 6 were approximately of thermal energy.

In the latest series of experiments, it was found more convenient to use electrically produced beta rays (2 m.e.v.) than pile radiations. Also the irradiations (unless otherwise noted), were conducted in the absence of appreciable amounts of water vapor and atmospheric oxygen. This was achieved by placing the yarn in glass tubes and evacuating the yarn on a specially designed high vacuum line down to a pressure of 1 μ or less.

With regard to the use of electrically produced beta rays in place of pile radiation, it was felt that the difference in origin of the radiation would have no measurable effect on the irradiation for the following reasons:

1. Beta rays and high speed electrons are physically identical, and the only difference between fission product radiation and the monoenergetic high speed electrons which were used is that the pile-produced rays have a statistical distribution in energy while the latter, as produced by the Van de Graaff generator, have all the same energy.

[1] Edward S. Gilfillan and Leo Linden, TEXTILE RESEARCH JOURNAL **25**, 773 (1955).

2. The density of ionization along a track is essentially independent of the energy (speed) of the moving electron, and for a given dose the total track length for the two velocity distributions is the same.

The facility for irradiating the samples was a 2 m.e.v. Van de Graaff particle accelerator. The primary beam from the generator, $\frac{1}{8}$ in. in diameter, was approximately cylindrical. The position of this beam in the plane of the target was varied by means of an electromagnet excited at 200 c.p.s., in such a way as to provide a substantially uniform scan on a line 8 in. long. The glass tubes containing the yarn samples were arranged on a conveyor belt with the axis parallel to the line of scan and were passed through the line of scan at a rate of 40 in./min. The voltage of the radiation and its amount in microamperes were read directly from the generator control panel.

It should be pointed out here that the interposition of glass between the radiation source and the sample produced changes in both the quality and quantity of the radiation. It slowed down all the incident electrons, but the total number of electrons reaching the yarn was increased over the number supplied by the generator. The increase was due to the secondary electrons that were dislodged from the glass by the primary beam.

Because of the curvature of the glass tubes, the electrons striking different portions of the tubes that contained the samples passed through different thicknesses of glass. Thus the dose from a single pass through the beam would be nonuniform. By taking into account the thickness and density of the glass, the width of the beam, the production of secondary electrons in the glass, and the scattering angle of the radiation, calculations indicated that if the tubes were rotated by 45° increments between passes, the irradiation would be uniform within 50% and probably considerably better. The beam voltage was maintained at 2 m.e.v. and the beam current at 287 microamperes except where otherwise noted. The calculated mean exposure was 4.7×10^6 r. equivalent in eight passes.

From the earlier work it was realized that the differences in some of the physical properties of the yarns might be small percentagewise after they were irradiated. Therefore great care was necessary to cancel out chance effects related to the history of the yarn if statistically significant results were to be obtained. Thus every sample irradiated was accompanied at all times by a blank which was treated identically except for the actual irradiation. In all cases, sample and blank were pumped together on the same manifold down to a pressure of 1 μ or less, as judged by the faintness of the glow discharge when the residual gas was excited by a high frequency electrical discharge. The sample and blank were held on the manifold at this low pressure for at least 4 hr. before they were sealed and removed.

Although the primary interest was to explore the effects on the irradiation of cotton caused by the presence of water vapor and atmospheric oxygen, a few additives were also included during several of the irradiations. These were applied to the cotton yarn while the yarn was in place in the vacuum system manifold line. When additives were used, pumping was a necessary preliminary to irradiation in order to ensure sufficient expulsion of water vapor and molecular oxygen. The basis of selection of additives was twofold: first, availability for cross-linkage, and second, as an antioxidant—this time not as a bridging agent but rather to prevent the accumulation of appreciable concentrations of hydrogen peroxide.

With regard to cross-linkage, this of course would be desirable to improve such properties as strength and resistance to heat. It is assumed that cross-linkage is preceded by the activation of "available sites" on each of the two adjoining parallel cellulose chains, then followed by the formation of a chemical bond between these two sites. The question raised is whether or not it would help to have available in the vicinity a chemical bridging compound ready to slip into place. It was hoped to accomplish something like this by the use of petroleum ether and also carbon disulfide.

Presumably a carbon-carbon linkage across the two sites would form the strongest possible cross-link, and presumably the greater the number of carbon atoms in the straight-chain hydrocarbon bridge, the more flexible the cross-linked fibers would be. These considerations lead to the selection of petroleum ether. Should petroleum ether prove too inert to form the bridge in the very brief time during which the sites remain open after irradiation, a more reactive bridging compound could be substituted at the expense of a theoretical advantage of the carbon-carbon bridge. Vulcanization of rubber is known to be a cross-linking process; this suggested the use of a sulfur compound. Carbon disulfide was selected.

TABLE I. Effect of Irradiation on the Strength, Per Cent Water-Soluble Material, and pH of a 75/1 Cotton Yarn

Sample*	Single end strength, g.	Tenacity, g./den.	Loss in tenacity (based on blank), %	Water-soluble material, %	pH
Blank, pumped	157.3	2.22		2.26	6.52
Sealed but not pumped	93.9	1.44	35.2	3.02	6.08
Pumped	92.1	1.33	40.0	3.40	6.03
Carbon disulfide additive	110.0	1.56	29.7	3.17	6.10
Petroleum ether additive	100.0	1.42	36.0	3.25	6.05

* All samples except the blank were irradiated.

Procedure

As previously noted, the cotton, in yarn form, was irradiated in a beta ray field electrically produced by a Van de Graaff generator; 4.7×10^6 r., as measured at the cotton, were selected for the "standard" or full dose in this work. Later the dose was varied. In preparation for the irradiations previously described, the samples of yarn were wound under uniform tension onto brass tubes to a depth of approximately $\frac{1}{16}$ in. These were placed into cylindrical glass tubes and pumped (evacuated) when so indicated. The first series of samples (75/1 cotton—Table I) were placed in pyrex tubes; however, some of these were punctured by an internal voltage due to the accumulation of an electric charge inside the pyrex tube, and when it reached sufficient voltage, the charge sparked to the ground and ruptured the tubes. It was found that this difficulty could be eliminated either by sealing in an electrode to carry off the charge or by the use of soft glass tubes in place of the pyrex tubes (Table II). The latter method was adopted and was the method used in the final series of irradiation.

TABLE II. Effect of Irradiation on the Strength of a 30/1 Cotton Yarn, Pumped in Soft Glass, with and without Electrodes, Dosage 4.7×10^6 r.

Sample*	Single end strength, g.	Tenacity, g./den.	Loss in tenacity (based on blank), %
Blank, pumped	454.8	2.56	—
Not pumped	332.5	1.87	27.0
Pumped	320.0	1.81	29.3
Not pumped, plus electrode	332.3	1.82	28.9
Pumped, plus electrode	330.4	1.88	26.6

* All samples except the blank were irradiated.

In the final series (Table III), it was decided to stay with the "pumping" or "evacuating" even though the previous tests gave no indications that the presence of water vapor and/or atmospheric oxygen affected the strength of the cotton yarn during irradiation. The reasons for continuing the use of the pumping procedure were (1) in general the theory was sound; (2) pumped samples generally were not discolored after irradiation, whereas irradiated but unevacuated samples (unpumped) exhibited varying degrees of a yellow-brown discoloration, particularly at the higher doses.

Because of the rather limited amount of yarn available from any one run, the strength evaluations

TABLE III. Effect of Irradiation on the Strength of a 30/1 Cotton Yarn, Varied Dosages, with and without Additives

Sample*	Single end strength, g.	Tenacity, g./den.	Loss in strength (based on blank), %
Group 1, full dose, 4.7×10^6 r.			
Blank	471.0	2.52	—
Irradiated	319.0	1.79	29.0
Water-treated, blank	425.3	2.50	—
Water-treated, irradiated	374.1	2.08	16.8
Carbon disulfide-treated, Blank	459.0	2.54	—
Carbon disulfide-treated, Irradiated	357.6	1.88	26.0
Hydroquinone-treated, Blank	461.3	2.53	—
Hydroquinone-treated, Irradiated	405.7	2.13	15.8
Group 2, one-half dosage			
Blank	431.3	2.44	—
Irradiated	354.5	2.03	16.8
Group 3, one-fourth dosage			
Blank	436.3	2.52	—
Irradiated	389.9	2.20	12.8

* Blank samples pumped, but not irradiated. All other samples were pumped and irradiated.

were restricted to single end strength, "dry" at standard atmosphere, 65% R.H. at 70° F. A Scott IP_2 Single End Serigraph machine was used. Since products of degradation were our primary concern, the chemical evaluations consisted of

1. Per cent water-soluble material as determined by a standard boil-off.

2. pH determined by boiling the cotton yarns for 5 min. in distilled water and then checking the pH of the extract after it cooled to room temperature.

3. Specific tests for the presence of products of chemical degradation by means of Fehling's solution; relative affinities toward basic and direct dyes, including methylene blue absorption; and tests for the presence of water-soluble and/or insoluble oxidizing agents.

Discussion

Owing to the nature of the investigation, the first part of the discussion deals with the effect of the irradiations on the strength of the cotton yarns; this is followed by the results from the chemical tests, with discussions and conclusions confined to the obvious. However, it should be pointed out at this time, withholding the detailed discussion until later, that all of the irradiated samples showed definite chemical degradation, and the indications were that oxycellulose was by far the principal product.

As noted in a previous part of this report, the first run was with a 75/1 cotton in evacuated or pumped pyrex tubes. The results are summarized in Table I. For this particular series, per cent water-soluble material and pH were determined, and the results are also included in the table. The set of samples included the first experiments with the carbon disulfide and petroleum ether additives. The results were disappointing due to the fact that an accumulation of electrical charges produced violent sparking inside of the tubes which either cracked the tubes or blew off the tips. It was felt that the phenomena associated with this could have had adverse effects on the cotton yarns. Very briefly, the loss in tenacity ranged from about 30 to 40%, with an indication of a slightly lower loss of strength for the sample pretreated with carbon disulfide. There was no indication that evacuating the samples, i.e., the presence of water vapor and atmospheric oxygen, had any effect on the strength characteristics. However, the evacuated samples did show less discoloration than the samples which were sealed but not pumped.

With regard to per cent water-soluble material and pH, irradiation increased the per cent soluble material and apparently produced a slightly acid condition on the yarns.

The next series (irradiated under the same conditions as the first) was actually a trial run to check out several means of eliminating the build-up of electrical charges. The basic change was substituting soft glass tubes for pyrex, and also some of the tubes were equipped with electrodes to carry off the charges. It was found that the substitution of soft glass was all that was necessary. For this trial and subsequent runs a 30/1 cotton was substituted for the 75/1. In this particular series, evacuated and unevacuated samples were evaluated, and again the difference noted was the fact that the pumped samples exhibited much less discoloration than the unevacuated samples.

The only interesting fact to be gained from the strength characteristics of the yarns irradiated in the above manner is that the loss in tenacity was in the neighborhood of just under 30% and reasonably uniform considering the nature of the work, as against 30 to 40% for the first series irradiated under the same conditions. This would seem to indicate that the electrical charges encountered during the first run had degrading effects on the strength.

With the information gained from the two previous sets of irradiations, a third series of samples was prepared. These included, in addition to the standard and its corresponding blank the following samples:

1. Samples to which water was purposely introduced in liquid form to further check on the effects of the presence of water vapor.

2. Carbon disulfide additive. The first irradiations indicated that the inclusion of carbon disulfide might have some beneficial effects.

3. Hydroquinone. All of the tests run to date indicated the harmful effects due to the formation of oxidants during irradiation. It was expected that hydroquinone (an antioxidant) might prevent appreciable accumulations.

Finally, standard pumped samples were irradiated at about one-half dose and one-fourth dose, respectively. The standard dose adopted for this series of experiments with 4.7×10^6 r., as measured at the cotton. The beam voltage was 2 m.e.v. and the beam current 287 microamperes. The voltage was kept constant for the reduced runs; however, the beam

current was dropped first to 146 microamperes and then to 73 microamperes, which in effect reduced the dosage by about a half and then by about a fourth of the standard dose. The results of this run are summarized in Table III. At the full dose of irradiation the standard pumped sample and the carbon disulfide sample had the greatest loss in strength (25 to 30% range), with no indication that carbon disulfide was beneficial in this respect. At full dose, both the water-treated and hydroquinone-treated samples had a loss of about 15% and in this respect were at least as good as the standard-type sample which received one half the dose. This run also indicated, as expected, that the lower the dose, the lower the loss in strength due to irradiation. The water-treated and hydroquinone-treated samples apparently had beneficial effects. The advantage of the hydroquinone can be explained by the antioxidant theory; however, as of now there is no visible explanation for the encouraging results obtained with the water-treated samples.

Returning to the discussion of the chemical tests, it will be recalled that all the irradiated samples exhibited definite degrees of chemical degradation, with the indications that oxycellulose was the principle offender. Samples from all of the irradiation series were first treated in Fehling's solution. Only the irradiated samples exhibited the characteristic pinkish stains which indicate the presence of either hydrocellulose or oxycellulose. It is realized that the various complexities associated with and resulting from irradiation most likely produced more than one type of chemical degradation. However, based upon the fact that it is well-known that beta radiation produces hydrogen peroxide from moisture and produces ozone from atmospheric oxygen, it was felt that one type of degradation must have predominated. The method adopted to indicate the principle product was one of checking the affinity of the irradiated yarns in (1) methylene blue (basic dyes) and (2) direct dyes, before and after yarns were pretreated with a solution of sodium hydroxide. Again, it is realized that these techniques have limitations; however, due to the small amount of yarn available for these tests, it was felt that the method used would present at least rough qualitative representation.

The first step consisted of treating the control, blanks, and irradiated yarns in a 0.5% solution of methylene blue. All of the irradiated samples exhibited a much greater affinity for the dye than did the samples which were not irradiated. Now the greater affinity for the basic dye would seem to indicate either hydrocellulose (dried in acid type) or the acidic-type oxycellulose. To isolate the type still further, additional samples of all of the yarns (irradiated and nonirradiated) were pretreated first at the boil for 30 min. in a 0.5% solution of NaOH. Then pretreated and untreated yarns were dyed simultaneously with Pontamine Sky Blue 6BX (direct dye). In the untreated condition, the nonirradiated yarns exhibited a much greater affinity for the direct dyes than did the irradiated yarns. However, after the caustic pretreatment, the irradiated yarns regained their affinity for the direct dyes and dyed at least as heavy as the controls and blanks. By process of elimination, the reactions of irradiated yarns, first to methylene blue and then to direct dyes, would seem to indicate that the predominant product of degradation was the acidic-type oxycellulose. According to Doree in "The Methods of Cellulose Chemistry," Bunke and Wolfenstein examined the action of solutions of hydrogen peroxide on filter paper, and the result was a new product which they designated as "hydral" cellulose, which had properties very similar to those of an oxycellulose. Also, in the same book, Doree and Cunningham describe the action of ozone on moist cellulose. They indicate that ozone acting on moist cellulose produces acidity on the fiber and also that the first stage of the action of ozone results in the formation of cellulose peroxide. Thus from the nature of the irradiations and the history of the samples, it seems possible that the predominating product of degradation was caused either by peroxides and/or ozone resulting in the formation of cellulose peroxide. For an additional test to check the nature of the peroxides, water extracts of the various yarns were treated with a potassium iodide solution. The results were negative. Then, when the extracted yarns were treated, only the irradiated yarns exhibited a brown stain, indicating that iodine was liberated and that probably an oxidizing agent not present before irradiation had been formed. From the insoluble character of the agent, it was assumed that it was cellulose peroxide.

Out of curiosity alone, irradiated samples were dyed with an acid dye, Calcoid Navy Blue 3R, and also with the differential dyes Diphenyl Fast Red SBL and Chlorantine Fast Green BLL. The irradiated samples showed much less affinity toward

the acid dye than did the blanks and grey yarn "as received." With regard to the differential dyeing, the irradiated samples dyed red while the blank and control yarns, as received, dyed to the same color, namely, a grayish-purple.

Conclusions

Within the limitations imposed by investigations of this nature, the indications are

1. The presence of water vapor and atmospheric oxygen during irradiation has little or no effect on the strength of the cotton yarn.

2. Degradation products were formed by the irradiation, principally oxycellulose of the acidic type.

3. The irradiations produced an insoluble oxidizing agent, and based upon the insoluble character of the agent and the history and nature of the type of irradiations used, it is assumed to be cellulose peroxide. It is speculated that the peroxide polymer might have been formed from the hydroxyl groups present in dry cellulose.

4. The dosages of irradiation employed in these experiments significantly reduced the strength of cotton yarns. However, the inclusion of additives, such as antioxidants, might be employed to advantage, particularly at lower doses.

5. The irradiated cotton has lower affinity than normal for direct dyes, and greater affinity than normal for basic dyes. These characteristics were influenced by the large amounts of oxycellulose formed during the irradiations.

Acknowledgments

Through the cooperation of Davis Dewey III, Vice-President of the High Voltage Engineering Corp., Cambridge, Mass., the facilities of one of their Van de Graaff particle accelerators were made available for this study.

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Chemical Modification of Cotton by Reaction with Activated Olefinic Compounds

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CURRENT interest in the cyanoethylation of cotton with acrylonitrile, an activated olefinic compound, has prompted the authors to examine some similar unsaturated compounds which are available and which might be expected to react with cotton to give new and useful products. If the base-catalyzed Michael-type addition reaction with cellulose, which proceeds in the case of acrylonitrile, is a general one, it offers a convenient means of etherifying cotton under mild conditions. Such addition reactions should provide many useful derivatives of cellulose.

The present investigation was undertaken to determine if cotton fabric would react with a number of activated olefinic compounds in the presence of catalytic amounts of alkaline reagents to produce useful chemically modified cottons that are insoluble in water or in alkaline solutions. Results of a preliminary screening of compounds are reported here. A description of the preparation and properties of carbamoylethylated cotton obtained by reaction of cotton fabric with one of the compounds, acrylamide, will be reported in the April issue of the Journal.

[1] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U.S. Department of Agriculture.

Michael Reaction

The Michael reaction [6, 13] involves the conjugate addition of a compound containing active hydrogen to an alpha-, beta- unsaturated ketone, ester, amide, nitrile, nitroalkene, or sulfone in the presence of a basic catalyst. The catalyst functions

by removing a proton from the compound containing the active hydrogen, leaving an anion free to attack the beta-carbon of the unsaturated acceptor. In subsequent steps the catalyst is regenerated and the Michael aduct is formed. The reaction may be represented by the scheme shown in Figure 1.

Cyanoethylation is the general term employed to describe reactions in which acrylonitrile, $CH_2=CHC\equiv N$, adds compounds containing active hydrogen, such as compounds containing active methylene or methinyl groups, amines, phenols, hydrogen sulfide, and alcohols. It is considered a special case of the normal Michael condensation [1]. The literature also contains examples in which Michael acceptors other than acrylonitrile have undergone, in the presence of basic catalysts, addition reactions with compounds in which the active hydrogen involved is on the hydroxyl group of a primary or secondary alcohol [2, 14], polyhydric alcohol [4, 5, 16], thioalcohol [7], or thiophenol [12], rather than on a methylene group to which are also attached activator groupings such as $-CO_2R$, $-COR$, $-CN$, $-CONH_2$, $-NO_2$, $-SO_2R$, $-CHO$, etc., as in the case of classic Michael reactions. The scheme in Figure 2 illustrates a mechanism for the addition of an alcohol to a Michael acceptor in the presence of a basic catalyst.

The patent literature describes addition reactions of cellulose with alkyl acrylates [8], with acrylamide [3, 19], with alpha-, beta-unsaturated aldehydes [15], ketones [15], ethers [15], nitriles [15], carbodiimides [15], and polycarboxylic acid esters and salts [15], with monovinyl [18] and divinyl sulfones [17], with vinyl sulfonic acid [10], and with vinyl sulfonamides [9]. However, these reactions were carried out with cellulose in the form of alkali cellulose, and in general the products obtained were soluble. If such addition reactions of cellulose with activated olefinic compounds are regarded as Michael-type additions, it is possible that they may be carried out under mild conditions in the presence of alkaline reagents in catalytic amounts only, and may be expected to be governed by some of the general factors which influence the Michael reaction.

The extent to which a given Michael-type addition reaction will proceed depends on the following facts: (1) the reaction is a reversible one; (2) functional groups vary in their ability to activate the electrophilic activity of the double bond; and (3) substitution on the alpha- or beta-carbon of the acceptor usually results in lower reactivity toward a given addendum [6]. As an additional influence in the case of cotton cellulose, the heterogeneous nature of the reaction with the activated olefinic compound will tend to lower the reactivity.

In the preliminary study reported here, compounds were screened for reactivity toward cellulose under certain mild conditions, and no attempt was made to evaluate the influence of each of the above factors with respect to each compound.

Experimental

Materials

The compounds investigated in this study were acrylamide, acrylic acid, methyl acrylate, methyl methacrylate, N, N′-methylenebisacrylamide, N-tert.-butylacrylamide, maleic acid, fumaronitrile, crotonic acid, crotonaldehyde, itaconic acid and its dimethyl and diethyl esters, mesityl oxide, ethyl alpha-cyanocinnamate, and meta-nitrocinnamic acid.

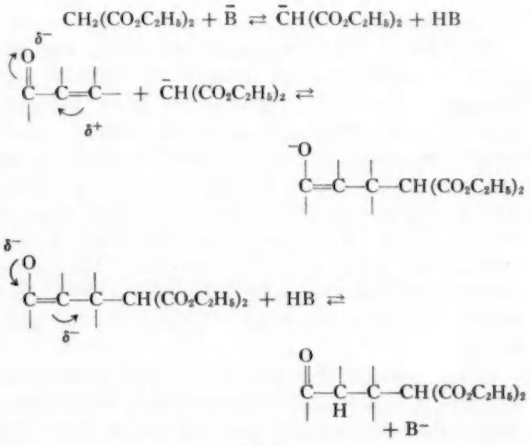


Fig. 1

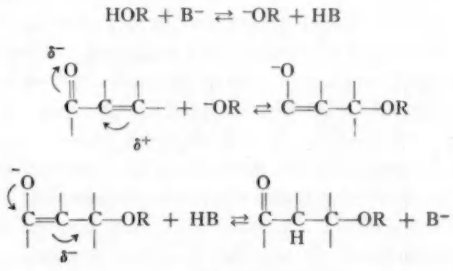


Fig. 2

The cellulose was in the form of 48 × 48 cotton sheeting which had been peroxide-bleached in a continuous range with caustic pretreatment.

Either sodium hydroxide or trimethylbenzylammonium hydroxide was used as catalyst, but other strong bases could be used.

Methods of Application

In each case, the reagent was brought into contact with cotton fabric in the presence of a base, and the fabric was heated.

Method A. If the activated unsaturated compound was water-soluble, the procedure involved impregnating the sheeting with an aqueous solution containing the reagent and the alkaline catalyst, passing the fabric through the squeeze rolls of a laboratory padder, drying and heating in a forced air oven, and washing in water.

Method B. With water-insoluble unsaturated compounds, the fabric was impregnated with an aqueous solution of the alkaline catalyst, sent through the squeeze rolls of a laboratory padder, and then heated with the compound either (1) in undiluted form or (2) in an organic solvent. Washing was with appropriate organic solvents and then with water.

Method C. With certain compounds, the procedure involved impregnating fabric with the unsaturated reagent, in solution or undiluted, then impregnating with the alkaline solution. Heating was in a forced air oven, and washing was with water.

Method D. In a few cases, sheeting was impregnated with an organic solvent containing both catalyst and reagent, sent through the squeeze rolls of a laboratory padder, heated in a forced air oven, and washed with organic solvents, then with water.

Tests

Treated fabrics were examined by means of analysis for substituent groups and dyeing characteristics to determine if reaction had occurred. When the activated unsaturated compound contained nitrogen, the treated cotton was analyzed for nitrogen. If the expected modification contained an acid group, the maximum ion-exchange capacity was determined in order to establish the degree of substitution [11]. Methylene Blue (a basic dye) was used in some cases to detect the presence of an acidic group. Ordinary cotton or chemically modified cotton containing basic groups are stained only slightly with the dye, but cotton modified with acidic groups accepts the dye. The degree of dyeing is related to the number of acidic groups present. A differential dye bath was used in a few cases to detect chemical modification. The differential dye bath contained approximately equal amounts of Pontamine Blue RRL 175%, a direct cotton dye, and Celliton Fast Yellow RRA, an acetate dye. Blocking of the cellulosic hydroxyl groups caused a resistance to the cotton dye and an affinity for the acetate dye. In all dyeing tests, blanks and catalyst-treated controls were dyed with the samples.

Application of Activated Olefinic Compounds to Cotton

Acrylic acid. The sodium salt of acrylic acid, $CH_2{=}CH\,C(=O){-}ONa$, reacted with cotton sheeting in the presence of sodium hydroxide. Application Method A was used. The aqueous solution contained 17.3% sodium acrylate, 4.2% sodium hydroxide, and a trace of p-phenylenediamine as polymerization inhibitor. Drying and heating was for 10 min. at 140° C. The product dyed a much deeper shade with Methylene Blue than the control fabric, and had an ion-exchange capacity of 150 meq./kg. This corresponds to a substitution of 1 carboxyethyl group per 40 anhydroglucose units. No attempt was made to determine conditions for maximum introduction of carboxyethyl groups into cellulose by reaction with the sodium salt of acrylic acid.

Methyl acrylate. There was a slight evidence of reaction with cotton when methyl acrylate, $CH_2{=}CH\,C(=O){-}O{-}CH_3$ (practical grade), was applied to sheeting using Method B. Sheeting impregnated with 5% aqueous sodium hydroxide solution was submerged in methyl acrylate from which the hydroquinone had been removed by extraction with sodium hydroxide solution. Since hydroquinone was found to discolor alkali-treated cotton fabric, 0.2% para-phenylenediamine was used as the polymerization inhibitor. The fabric was heated with the methyl acrylate at 73° C. for 2½ hr. Washing was with 95% ethanol and with water.

A small weight increase, 3.6%, was observed in the fabric, which dyed a deeper shade with Methylene Blue than appropriate controls and a much deeper shade after boiling in 5% sodium hydroxide

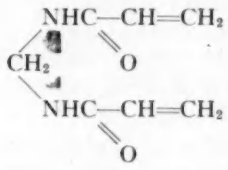
to hydrolyze more of the ester groups. This slight degree of reaction of methyl acrylate with cotton might possibly be increased by varying the conditions of treatment.

Methyl methacrylate. A 5% solution of trimethylbenzylammonium hydroxide was the catalyst used in treating fabric with methyl methacrylate, $CH_2{=}C(CH_3){-}C(=O){-}OCH_3$, by Method B. Catalyst-impregnated fabric was heated at 70° C. for 1 hr. with methyl methacrylate to which 0.2% paraphenylenediamine had been added as an inhibitor to replace hydroquinone, which had been removed by extraction with dilute sodium hydroxide solution. Washing was with 95% ethanol and with water. The fabric showed a weight increase of 3.1%. However, Methylene Blue dyeing gave no evidence that reaction had occurred. The treated fabric dyed the same shade as the control samples, both before and after boiling in 5% sodium hydroxide for ½ hr. This would indicate that the methyl methacrylate did not react with the cotton by addition across the double bond.

Acrylamide. Cotton fabric reacted with acrylamide, $CH_2{=}CHC(=O){-}NH_2$, to give a carbamoylethylated product which may be represented by the formula cellulose$-O-CH_2CH_2C(=O)-NH_2$. In this instance 80×80 print cloth was used. Method A was employed, with the aqueous treating solution containing 12.6% acrylamide and 3.8% sodium hydroxide, and with heating at 125° C. for 6 min. The treated fabric contained 1.41% nitrogen, which corresponds to a substitution of 1 carbamoylethyl group per 5.7 anhydroglucose units. The product dyed slightly darker than control fabric with Methylene Blue. Some of the carbamoylethyl groups were hydrolyzed by allowing the treated fabric to soak in 0.5% sodium hydroxide solution for approximately 72 hr. The alkali-soaked product after thorough washing, dyed a deeper shade with Methylene Blue than it had dyed before the prolonged exposure to sodium hydroxide.

Since acrylamide reacted readily with cotton fabric, further study of the carbamoylethylation of cotton was carried out. Details on the preparation and properties of carbamoylethylated cotton will be reported in the April issue of the Journal.

N,N′-Methylenebisacrylamide. Reaction occurred when cotton fabric was treated according to Method A with N,N′-methylenebisacrylamide,

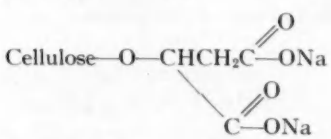


The treating solution contained 15% of the unsaturated compound, 5% sodium hydroxide, and 0.16% para-phenylenediamine, and heating was for 10 min. at 115° C. The treated fabric had a full, soft hand, and showed a weight add-on of 4.9%. Nitrogen content of the fabric was 0.97% which represents a substitution of one methylenebis-(carbamoylethyl) group per 17 anhydroglucose units.

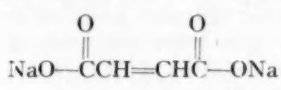
N-tert.-butylacrylamide. No reaction was observed when fabric was heated with N-tert.-butylacrylamide according to Method D. The treating solution contained 12.5% of the unsaturated compound, 6.2% trimethylbenzylammonium hydroxide, and 81.3% tert.-butanol, and heating was for 15 min. at 140° C. No nitrogen was found in the sample on analysis.

Treatment Method C was no more effective than Method D in attempting to react N-tert.-butylacrylamide with cotton fabric. Sheeting, padded with a 20% solution of the compound in tert.-butanol, air dried for 10 min., padded with 5% aqueous sodium hydroxide solution, heated for 10 min. at 115° C., and washed, contained less than 0.1% nitrogen.

Maleic acid. Cotton fabric reacted readily with the disodium salt of maleic acid to give a derivative which may be represented as



Fabric treated using Method A, with an aqueous solution containing 48% disodium maleate,



and 4.8% sodium hydroxide, with heating at 115° C. for 5 min., dyed a very deep shade with Methylene Blue both before and after being boiled in 5% sodium hydroxide solution, which indicates that a stable ether linkage had been formed. The fabric showed a distinct resistance to the direct cotton dye and a slight affinity for the acetate dye in the mixed dye bath. The behavior of the fabric closely resembled that of carboxymethylated fabric which was dyed in the same bath.

More extensive reaction occurred when the heating temperature was raised. Fabric samples treated according to Method A using a solution containing 20.4% disodium maleate and 4% sodium hydroxide, with heating at 125° C. for 10 min. in one case and at 140° C. for 10 min. in another, showed ion-exchange capacities of 226 meq./kg. and 243 meq./kg., respectively. These figures correspond to substitutions of 1 carboxyl group per 27 anhydroglucose units and 1 carboxyl group per 25 anhydroglucose units, respectively. Both of these fabrics dyed very dark shades with Methylene Blue, and exhibited a strong resistance to a direct cotton dye, Chlorantine Fast Blue 3 GLL.

Fumaronitrile. Samples of sheeting which were treated according to Method A, using aqueous solutions containing 12.5–15% fumaronitrile, N≡CCH=CHC≡N, and 3.5–4.4% sodium hydroxide, with heating at 115° C. for 5–10 min., dyed darker shades with Methylene Blue than did control samples. This indicates that reaction with the cellulose had occurred, and that some of the nitrile groups had been converted to carboxyl groups. However, the number of nitrile groups introduced was quite small; nitrogen values for the samples ranged from 0.19% to 0.26%. It is possible that with carefully controlled conditions the extent of reaction might be increased without hydrolysis of the nitrile groups.

Crotonic acid. A number of unsuccessful attempts were made to react crotonic acid,

$$CH_3CH{=}CHC(=O){-}OH,$$

with cotton. Both Method A and Method C were tried. With Method A, the acid was used in four different ways: (1) as the sodium salt without catalyst, (2) as the salt with 3.5% sodium hydroxide as catalyst, (3) as the salt with 16.4% sodium hydroxide as catalyst, and (4) in the presence of trimethylbenzylammonium hydroxide as catalyst. Heating was varied from 5 min. at 115° C. to 15 min. at 145° C. No evidence of reaction was obtained in any of the experiments as determined by Methylene Blue dyeing or weight increase.

With Method C, the aqueous treating solution contained the crotonic acid as such, as the sodium salt, or as the sodium salt in the presence of 4% excess sodium hydroxide. After drying for 2 min. at 140° C., fabric was padded with aqueous sodium hydroxide, the concentration of which was varied from 5 to 20%, and heated for 4 min. at 140° C. No evidence of reaction was indicated on dyeing these samples with Methylene Blue.

Crotonaldehyde. An orange-colored derivative which may be represented as

$$\text{Cellulose—O—}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{CH}_2\text{CHO}$$

was obtained when crotonaldehyde was reacted with cotton fabric. Method B was used, with 5% sodium hydroxide in the catalyst solution. The crotonaldehyde was cooled to 10° C. before impregnating the alkali-wet fabric with it. Heating was at 115° C. for 5 min. Washing was with 95% ethanol and with water, with subsequent extraction with 95% ethanol in Soxhlet extractors until no more color was removed. The fabric had a bright orange color, and did not appear to be stiffened.

The presence of aldehyde groups was demonstrated by the fact that the fabric reduced Fehling's solution. Equal portions of crotonaldehyde-treated fabric and sodium hydroxide–treated control fabric were heated in 50-ml. portions of Fehling's solution 26 min. from boil. After samples were thoroughly washed and dried, maximum ion-exchange capacity [11] was determined, using the sodium hydroxide–treated, Fehling's solution–treated control as a blank. The crotonaldehyde-treated fabric after oxidation with Fehling's solution showed an ion-exchange capacity of 192 meq./kg. which corresponds to a substitution of approximately 1 carboxyl group per 31 anhydroglucose units, and dyed a deep shade with Methylene Blue.

Itaconic acid and its esters. In the reaction of cellulose with itaconic acid, $CH_2{=}C(COOH)CH_2COOH$, trimethylbenzylammonium hydroxide was found to be a more effective catalyst than sodium hydroxide. Fabric treated according to Method A with an aque-

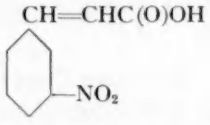
ous solution containing 15% itaconic acid and 6% trimethylbenzylammonium hydroxide and heated at 140–145° C. for 15 min. exhibited a slight weight increase and changed dyeing characteristics. The fabric dyed a much deeper shade with Methylene Blue than the control fabrics, and showed an almost complete resistance to both the cotton and the acetate dyes in the mixed dye bath.

Methylene Blue dyeing indicated that little reaction with the cotton occurred when fabrics which had been treated, using Method A, with solutions of disodium itaconate (20.1–46.8%) in dilute (1.7–4.5%) sodium hydroxide solutions were heated 5 min. at 115° C. or 30–60 min. at 150° C.

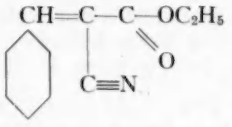
The dimethyl and diethyl esters of itaconic acid are insoluble in water. Fabric impregnated with 5% sodium hydroxide solution and heated for 1 hr. at 80° C. with undiluted dimethyl itaconate according to Method B dyed the same shade with Methylene Blue as the sodium hydroxide–treated control.

Diethyl itaconate was applied to fabric using Method D. The treating solution contained 15% diethyl itaconate, 14.4% water, 6% trimethylbenzylammonium hydroxide and 64.6% tert.-butanol, and heating was for 15 min. at 140–145° C. Methylene Blue dyeing before and after boiling for ½ hr. in 5% sodium hydroxide indicated that no reaction had occurred. Weight increase was negligible.

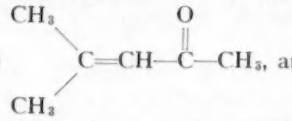
Meta-nitrocinnamic acid and ethyl alpha-cyanocinnamate. No reaction was obtained when fabric which had been impregnated with 5% trimethylbenzylammonium hydroxide solution was treated in a refluxing solution containing 10% meta-nitrocinnamic acid



in tert.-butyl alcohol. No reaction was observed when fabric which was wet with 5% sodium hydroxide solution was impregnated with an 18% solution of ethyl alpha-cyanocinnamate



in tert.-butanol then heated at 115° C. for 5–10 min. Use of the 5% sodium hydroxide solution as an aftertreatment according to Method C was also unsuccessful in promoting reaction of the ethyl alpha-cyanocinnamate with cellulose. The fabrics treated with these compounds showed no changed dyeing characteristics, and only traces of nitrogen, 0.03–0.08%.

Mesityl oxide. Fabric which had been swollen in 25% sodium hydroxide solution, then allowed to stand for 3 hr. in contact with a mixture of mesity oxide  , and ice retained a yellow color after extensive washing, and showed a weight add-on of 3%. A yellow-colored fabric having no apparent weight increase was obtained when Method A was employed, using 4% sodium hydroxide, impregnating the alkali-treated fabric with mesityl oxide, and heating for 5 min. at 115° C. No weight increase was observed when fabric was treated according to Method C, impregnating the fabric with undiluted mesityl oxide, then impregnating with 5% sodium hydroxide solution, and heating for 10 min. at 115° C.

Discussion

In the list below the activated olefinic compounds studied are grouped as to solubility in water and given the following rating: *X* if the reaction was extensive under the conditions noted; *Y* if some reaction occurred, as noted by changed dyeing characteristics or analysis; *Z* if no evidence of reaction.

Water Soluble

Acrylamide	*X*
N,N′-Methylenebisacrylamide	*Y*
Acrylic acid	*Y*
Maleic acid	*Y*
Itaconic acid	*Y*
Crotonic acid	*Z*
Fumaronitrile	*Y*

Water Insoluble

Methyl acrylate	*Y*
Methyl methacrylate	*Z*
Mesityl oxide	*Z*
Crotonaldehyde	*Y*
Dimethyl itaconate	*Z*
Diethyl itaconate	*Z*
N-tert.-Butylacrylamide	*Z*
Ethyl alpha-cyanocinnamate	*Z*
m-Nitrocinnamic acid	*Z*

As may be seen from this list, a variety of activator groupings are represented among those compounds which gave some evidence of reaction with cellulose: amide, acid, ester, nitrile, ketone, and aldehyde. However, acid, ester, and amide groups are also represented among the compounds which did not react under the conditions cited. For example, acrylamide reacted readily and extensively and N,N'-methylenebisacrylamide reacted to some extent, while N-tert.-butylacrylamide is apparently much less reactive.

It can be noted that both water-soluble and water-insoluble compounds showed some reaction, although for practical use the compounds which can be applied to fabric from aqueous solution would probably be most desirable. Crotonic acid was unique among the water-soluble acids studied in its failure to react with cellulose under the conditions of these experiments.

On the basis of the limited conditions studied for each compound, it would be unwise to make assumptions as to the effects of water solubility, substitution on alpha- or beta-carbons, and relative strengths of various groups in activating the unsaturated linkages. A more detailed study of the effect of conditions of treatment would be necessary before the reactivity of specific compounds toward cellulose could be predicted.

However, the general base-catalyzed reaction of cellulose with compounds having activated, olefinic linkages may be expected to yield useful cellulose ethers containing various reactive groups. The carbamoylethyl ether of cellulose prepared by this reaction has good fabric properties and modified dyeing characteristics. The cellulose derivatives of maleic, acrylic, and itaconic acids have changed dyeing characteristics and possess ion-exchange properties. The reaction product of cellulose with crotonaldehyde contains aldehyde groups which offer possibilities for further useful modification.

Summary

Preliminary experiments reported here indicate that compounds having olefinic linkages in conjugation with strongly electronegative groups vary widely in the ease with which they etherify cellulose in a base-catalyzed addition reaction. The reaction may have rather wide application in producing useful cellulose ethers, but the conditions for reaction with cellulose are somewhat specific for each compound.

Acrylamide reacted with cellulose readily. Maleic acid and acrylic acid reacted with cotton, but required higher temperatures than used for the production of carbamoylethylated cotton. The reaction of itaconic acid with cotton was almost negligible when sodium hydroxide was used as catalyst, but was extensive enough to change the dyeing characteristics of the cellulose when trimethylbenzylammonium hydroxide was used as catalyst. Neither sodium hydroxide nor trimethylbenzylammonium hydroxide was effective as a catalyst to promote reaction of crotonic acid with cellulose; no reaction was obtained even at elevated temperatures. Under conditions reported here, fumaronitrile reacted with cellulose to a slight extent, and changed the dyeing characteristics of the fabric. N,N'-methylenebisacrylamide reacted with cotton, but to a much smaller extent than acrylamide.

Of the water-insoluble compounds investigated, methyl acrylate, methyl methacrylate, and mesityl oxide produced slight weight increases, but little other evidence of reaction. Crotonaldehyde reacted with the cellulose, as evidenced by the presence of aldehyde groups in the treated fabric. Dimethyl itaconate, diethyl itaconate, N-tert.-butylacrylamide, ethyl alpha-cyanocinnamate and meta-nitrocinnamic acid gave no indication of reaction under the experimental conditions used.

Acknowledgment

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The Detection of Fungal Growth in Cellulosic Textiles

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Abstract

A staining test has been developed for the detection of the presence of fungal hyphae in cellulosic fibers. It is a modification of the Pianese IIIb test and depends on a simple differentiation in color between fungal hyphae and substrate. The test can be used to detect superficial growth, or more deep-seated growth such as that associated with the cellulolytic breakdown of the fiber. The test has been found to be successful over a range of cellulosic fibers, including dyed fibers. It may be of use in estimating the degree of maturity in cotton and in detecting the presence of fungal damage in raw cotton. A survey of previously described staining methods for the detection of microbiological damage is given.

Introduction

General Considerations

The recent increase in information on the extent of damage which results from microbiological attack on textile materials makes it apparent that this type of damage, once considered to relate largely to outdoor exposure under tropical conditions, does in fact operate in any location in which the necessary conditions of temperature, relative humidity, and contamination are present.

It is doubtless true that, with time, increasing use will be made of fibers which are inherently resistant to this type of attack, but it would be premature to assume that this trend, logical enough where practical and economic considerations warrant, would, in the near future, result in the replacement of the presently used fibers, of which cotton is the most important.

A voluminous literature in the field of textile microbiology has appeared in the past decade and this has dealt with both the fundamental and practical aspects of the matter. That portion dealing with cellulosic materials has recently been reviewed by Siu [30].

In many—possibly in most—of its manifestations,

microbiological attack on textile and related materials is readily recognizable. Certainly this is true in the case of fungal attack where it is usually possible to observe the presence of fungal hyphae and, sometimes, of spores on or in the fibers in the damaged areas of the material under study and to relate this to other characteristics such as discoloration, or loss in strength, in order to decide whether the attack is superficial or more deep-seated. However, it is sometimes necessary to obtain unequivocal evidence regarding the presence or absence of destructive microbiological attack in cellulosic fibers in the comparatively few cases where gross evidence of the presence of the organism is lacking. In such cases, recourse is usually had to one or another of a number of techniques involving staining, with or without prior swelling of the fiber.

It will be obvious that in cases of this kind it is not sufficient merely to establish the presence or absence of, say, fungal hyphae in admixture with the fibers in question. It must be shown that structural damage to the fiber cell or filament has, in fact, occurred, and that this is related to the presence in, or near the damaged areas, of fungal hyphae. Most convincing of all, in the case of fibers containing a lumen, is the presence of hyphae within the latter. Moreover, with the naturally occurring cellulosic fibers, where staining techniques are used, the accuracy of the observations should not be vitiated by interference by such naturally occurring bodies as heavily lignified or immature cells.

Bacterial attack is more difficult to identify because of the smallness of the organisms involved and their more uniform morphology in comparison with fungi. Many of the cellulolytic bacteria are anaerobic and this, together with the fact that textiles are less frequently exposed to attack under anaerobic conditions, has served to limit the number of investigations in the field of bacterial attack on cellulosic textiles.

In general, then, the problem of detecting microbiological attack in textile materials is one which can be regarded as relating to the detection of the presence of fungi, rather than bacteria; and while in most cases the detection of the damage is not difficult, there are some instances in which the detection of damage and the relating of it to the organisms responsible, involve the use of special techniques.

The work reported here falls in the latter category and was originally undertaken in an attempt to determine the extent to which microbiological damage could be detected in the fabric of the unlined flax fire hose used by Canadian forestry fire protection agencies. A summary of the background of the problem as it relates to this type of hose has been given in a previous publication [28]. In view of the fact that a similar need can arise in the case of textile cotton and other cellulosic textile fibers, the scope of the study has been extended to include some work on these.

Microbiological Damage in Raw Cotton and Other Cellulosic Fibers in the Natural State

Another field in which the investigation of staining techniques appears to be of interest is that which relates to the microflora of raw cotton and other cellulosic fibers in their natural states.

Marsh and Bollenbacher [21] have investigated the various types of fungi found on raw cotton which had undergone weathering in the field prior to harvesting and have shown that the ones most commonly present are various species of genera *Alternaria, Cladosporium,* and *Fusarium.* The same organisms were also present on dew-retted flax and hemp. Species of *Aspergillus, Penicillium, Stachobotrys,* and *Chaetomium* were reported on cotton and other fibers which had been subjected to humid storage.

In a later paper [22] the same authors give a critical survey of the literature dealing with the cellulolytic properties of the fungi found on cellulosic fibers and also include the results of their investigation of the cellulolytic properties of some 400 fungus isolates. They conclude that cellulose-destroying activity, while not universal, is very widely distributed among the fungi, occurring with a high degree of regularity among isolates of the genera *Alternaria, Chaetomium, Curvularia, Fusarium, Gliomastix, Helminthosporium, Humicola, Memnoniella, Stachobotrys,* and *Trichoderma;* also in some species of *Aspergillus* and *Penicillium;* not at all in *Mucor* and *Rhizopus;* and only rarely in the actinomycetes. This list of cellulolytic organisms is a large one and includes many of the organisms known to be present in cellulosic fibers in their natural state.

It is therefore apparent that cellulosic fibers such as cotton and flax can become infected with fungi, during the latter stages of growth and during harvesting in the case of cotton, or in the case of flax, during retting, and that some of these organisms

may subsequently, under suitable conditions, cause damage.

This is an aspect of cellulose fiber technology to which comparatively little attention has been paid. Fibers such as cotton and flax are frequently processed into yarns and fabrics without having received any treatment such as scouring or bleaching, which would destroy cellulolytic organisms associated with them. It is only necessary to subject such fibers, or the textile materials made from them, to suitable conditions of temperature and relative humidity to create the danger of microbiological attack by the organisms with which they are infected.

Reference should also be made, in this connection, to the work of Elting. This worker has shown [11] that raw cotton fiber which had been exposed, in the field or after harvesting, to the action of cellulolytic fungi showed a deterioration in quality upon storage and used the term "cavitomic" to refer to cotton in this condition. Elting also claimed that certain chemical tests, e.g., for pH and reducing sugars, could be used to determine fairly conclusively whether or not the cotton had been damaged in this way. Further data on the deterioration which this effect produces in cotton fiber properties were obtained by Wakeham, Stickley, and Spicer [35] who claimed that cotton showing this effect produced more processing waste, and gave weaker and less even yarns and more end-breakage in spinning. These authors also claim that the measurement of number-length distribution based on single-fiber length measurements, clearly revealed the cavitomic effect.

It will be obvious from these observations that as the danger of the above type of damage becomes more widely realized there will be an increasing interest in methods for readily demonstrating the presence of fungi in cellulosic textile fibers and for assessing possible damage. The modified Pianese IIIb test described in this paper is believed by the authors to be a useful addition to the various tests currently in use for this purpose.

Survey of Literature on Staining Techniques

A brief resume of the literature on the use of stains, with particular reference to the detection of microbiological damage in cellulosic textiles, is given in this section.

The literature on this subject may be divided conveniently into two broad classes, viz., that arising from purely biological studies and relating to the presence of fungi in plant or animal tissue, without specific reference to textile fibers, and that dealing with the recognition of these organisms in textile materials. The literature summary which follows is based on this division. The techniques described fall into two general categories viz., those involving a combination of swelling and staining the tissues under examination and those based on staining alone.

In the essentially biological field, Pianese [24], investigating the histology and etiology of carcinoma cells, made use of a mixture of Malachite Green, Acid Fuchsin, and Martius Yellow in aqueous alcohol. The specimen is stained with the above mixture, dried in absolute alcohol, and mounted in balsam. This stain was later used by Muller [23] in a study of cytoplasmic structure in plant cells and by Vaughan [34] for identifying fungus and host cells, respectively. This latter author points out that this stain was a useful one in differentiating the fungal hyphae from the plant substratum, this differentiation occurring in lignified and unlignified cell walls, both of which were stained green, the fungal hyphae being stained pink. This stain was also used by Johansen [18] in studies on the morphology of fungi. Stoughton [32] used thiamin and Orange G in pathological studies on plants, and Stanier [31], studying cytophaga on a cellulose substrate, reviewed earlier tests and expressed a preference for Winogradsky's [36] mixture of phenolerythrosin followed by dilute aqueous Gentian Violet, which colored the organisms, leaving the fibers colorless. Reference should also be made in this section to further procedures given in reference textbooks dealing with microscopy and microtomy, as for example, the ones by Lee [19] and Conn [7].

Prior to 1920 the literature in the field of textile microbiology includes a number of more-or-less sporadic references to known or suspected cases of mildew attack on textile materials. Many of these relate to the growth of microorganisms in yarn-sizing preparations. They go back to the time of Witz [37] who describes the decolorization, produced in cotton printed with Ultramarine Blue, and resulting from the growth in the fabric of acid-producing fungi. In 1920 Thaysen and co-workers [12] described a test for detecting fungal damage in cotton fibers involving swelling the fiber in a mixture of carbon bisulphide and aqueous sodium hydroxide. This test was later examined critically by

workers at the Shirley Institute, in particular by Denham [9], who pointed out that the test depends on the behavior of the cell cuticle under the action of stresses produced by the swelling of the wall layers, and hence that slight mechanical damage to the cuticle, e.g., in ginning, may produce fallacious results. Denham obtained confirmation of this view in a critical examination of infected and normal cotton fibers. Clegg [5], another Shirley worker, described a general test, involving swelling the fiber in aqueous sodium hydroxide followed by staining with Congo Red, for detecting various types of damage in cotton fibers, including that caused by fungi and bacteria. This valuable test has been widely used by other workers. Hall and Elting [16] experimented with Methyl Violet applied to fibers previously swelled in sodium hydroxide and found that the fungal hyphae were stained purple, while the cotton fibers were unstained. Prindle [26] used a technique involving swelling the fiber in cuprammonium followed by staining with "Victoria Blue" although the particular Victoria Blue used is not indicated.

Numerous workers have made use of techniques involving staining alone for revealing the presence of microorganisms on cotton fiber in cases of known or suspected damage. Trotman and Sutton [33] showed that raw cotton attacked by bacteria had an increased affinity for Benzopurpurin. Armstead and Harland [1] using "Cotton Blue," found that in cotton fabric attacked by *Penicillium* and *Aspergillus*, the hyphae were stained more heavily than were the cotton fibers. The particular type of Cotton Blue used is not indicated. Similar results were reported by Bright [3] and Galloway [13]. Chace [4] studied the use of various Cotton Blues and also experimented with differential color filters for improving the contrast between the fungal hyphae and the fiber. Winogradsky [36], in a study of soil microbiology, used Acid Erythrosin followed by aqueous Gentian Violet to indicate the presence of bacteria on cotton fibers, the organisms being stained and the fibers not. Jennison [17] seems to have been the first to apply the Pianese IIIb technique to cotton fiber weakened by fungal attack and used this procedure as a preferred alternative to the Cotton Blue method; but this work does not seem to have been followed up by other workers in the textile field. Shchepkina [29], in a study of the internal microflora of the cotton fiber, describes a technique for staining using a phosphate buffer mixture followed by Bromphenol Blue. Rogers, Wheeler, and Humfeld [27] describe a procedure using Basic Fuchsin followed by aqueous phenol which colors the hyphae pink and does not color the cotton.

Experimental

I. Examination of Some Currently Used Staining Techniques

Three staining techniques in current use for detecting microbiological deterioration, viz., the Methylene Blue, Congo Red, and Basic Fuchsin tests were compared with the Pianese IIIb test, as modified in the present study, with respect to accuracy of interpretation and convenience. The cellulosic materials used in the tests were unbleached and bleached cotton which had undergone outdoor weathering, unbleached cotton, and flax forestry fire hose fabric which had been damaged by microorganisms in soil burial tests. In the case of the latter samples two general series of tests were carried out, the first on freshly damaged specimens and the second on samples which had been damaged several years before.

Samples showing mechanical damage were prepared by abrading fabric on a Taber Abraser. Chemically damaged specimens of cotton which had undergone hydrolytic attack by sulfuric acid and oxidative attack by alkaline hypochlorite and by hydrogen peroxide were also employed.

The dyes used in these tests were obtained from the Pharmaceutical Laboratories, National Aniline Division, Allied Chemicals & Dye Corp., 40 Rector St., New York 6, N. Y., and carried the certification data shown in Table I.

A. *Methylene Blue test* [3, 9]. To prepare the stain, 1 g. Methylene Blue chloride was dissolved in 100 ml. methanol and 1 ml. 3 *N* sulfuric acid added with stirring. After standing, the solution was filtered through glass wool to remove any sediment.

TABLE I. Certification Data for Dyes Used

Dye	Certification No.	Colour index No.	Total dye content, %
Methylene Blue chloride	NA 29	922	86
Congo Red	NQ 15	370	91
Martius Yellow	NYM 5	9	88
Malachite Green	NMg 17	657	99
Acid Fuchsin	NR 29	692	59

The fibers were mounted dry under a cover slip and a drop of the stain added at the edge of cover slip. The slide was placed in an oven at 40° C. for 3 min. to remove alcohol. Excess stain was removed by drawing distilled water through the mount by means of filter paper.

Further elaboration of the Methylene Blue test involving the use of sodium zincate has been developed [20, 25] to increase the specificity of the test with respect to various types of damage. This involves displacing the Methylene Blue solution with a solution of sodium zincate, followed by displacement of the sodium zincate by water, the appearance of the fiber being noted after each step. These additional procedures were carried out, and the data obtained are given in Table II.

Considering the extent to which the test distinguishes between microbiological and other types of damage, it will be seen that it does not, at any stage, permit a distinction between microbiological and mechanical damage but can, in its two latter stages, distinguish between these types and chemical damage. Since in the problems which arise, the need for distinguishing between microbiological and mechanical damage is of prime importance, and since it is generally not difficult to detect chemical damage, it will be seen that the test does not meet the need.

B. *Congo Red test* [5, 6]. The basis of this test is the different rates of diffusion of the dye into the cuticle and the exposed secondary cellulose of the fiber. The fiber is swollen first in sodium hydroxide solution, which brings about extension of the breaks where the cuticle is damaged. When the secondary cellulose is exposed as a result of the cuticle damage, or at a base or broken end of a fiber, the fiber is not uniformly colored. The cuticle stains only a faint pink, but the stain is taken up more rapidly by the secondary cellulose, which becomes bright red in color.

The procedure consists of immersing the specimen for 3 min. in a 11% solution of sodium hydroxide, after which the specimen is thoroughly washed in distilled water, the water being removed by squeezing between filter papers. It is then placed for 10 min. in a saturated Congo Red solution, then rinsed as before, and finally immersed in 18% sodium hydroxide solution, which produces in the stained fibers a final swelling which accentuates the color contrast.

The observations made were in agreement with those given by Clegg. Undamaged fibers stained uniformly pink. In mechanically damaged fibers, the fiber surfaces showed bruising and abrasion with deep cuts in the fiber wall. In chemically damaged fibers, spirals and transverse fissures and cracks were

TABLE II. Results of Methylene Blue Tests on Cotton Fibers Damaged in Different Ways

Type of damage	1 Methylene Blue alone	2 Methylene Blue followed by sodium zincate	3 2 followed by water rinsing
A None	Stained medium blue.	Stained pale purplish pink. Straightening and some swelling. Cuticle intact and fiber outline clear. Fiber ends show dumbbell shape.	Stained medium blue as in 1.
B Microbiological	Stained medium blue. Ragged ends with cracked or roughened cuticle.	Stained pale purplish pink. Split ends, cracks, segmentation, and sometimes disintegration.	Stained medium blue. Effects shown in 2 somewhat more pronounced.
C Mechanical	Ditto	Ditto	Stained medium blue. No further change.
D Chemical	Stained light to dark shades of blue, depending on type of chemical used.	Stained pale purplish pink. More swelling than in undamaged. Cracks and deep incisions in cuticle. No dumbbell effect.	Stained as in 1. Extensive swelling and complete disintegration where damage severe.
Conclusions	No distinction on color basis and none between B and C.	Distinction on color basis only for certain types of chemical attack. No distinction between B and C, but some distinction between these two and D.	Color distinction as in 2. No distinction between B and C, but good distinction between these two and D.

evident, with breaks frequently occurring at these locations, and the fiber being unevenly red. In fibers which had undergone microbiological attack, the effects were occasionally similar to mechanical damage, but more commonly, as noted by Clegg, the effect was one of spiral splitting, comparable to chemical damage, and the fibers also showed the characteristic disintegrated appearance. Fungal hyphae stained a deep red. Their presence would aid in the decision as to the type of damage, although, as is the case in all tests in which the presence of biological residues is revealed, if the fungus is not of the cellulolytic type, damage to the fiber may be wrongly attributed to this cause. As further pointed out by Clegg, if hyphae are not present, other tests such as cuprammonium fluidity determination are necessary before conclusions can be drawn.

There is no doubt that the Congo Red test has served an extremely useful purpose in distinguishing between the various types of damage which textile materials suffer in use. Probably its greatest use has been in the household and garment textile field where it has been helpful in numerous investigations in which it has been necessary to distinguish between mechanical injury (including abrasive wear) and various types of chemical damage. Regarding its ability to distinguish between mechanical and biological damage, it would seem that where the damage is of biological origin, the test sometimes gives an appearance similar to that shown by mechanical damage, although this similarity becomes less with intensification of the biological damage.

C. *Basic Fuchsin test* [27]. Microbiologically damaged fibers were immersed in a 0.1% Basic Fuchsin solution in 95% ethanol. They were withdrawn and placed in a 1% aqueous phenol solution. The fibers were so pale a purple color as to be nearly colorless, and the fungal hyphae were pale pink or purple. Where balsam was used for a more permanent mount, the color was even less intense, the fibers being colorless and the hyphae straw-colored or pale pink. The technique is simple, but a greater difference in color between host and fungus is desirable, such as might be obtained by counterstaining [10].

II. The Modified Pianese IIIb Test

One of the authors (B. J. Gardner, unpublished data) had made use of this staining technique in detecting the incidence of moulds in plant tissues. This, together with the fact that earlier work of other investigators suggested that this technique might be suitable for the purpose in hand, prompted a critical examination of the method.

This test gives a differential staining of the fungal hyphae cells and those of the cellulose substrate, the former being stained red and the latter green. It seemed possible that this effect might be related to the presence of chitin in the fungal cells, since this substance contains a partially substituted amine group and would therefore be expected to combine with acid dyes, such as Acid Fuchsin. It was found that purified chitin stains a red color with Pianese IIIb stain.

Because of the clear-cut color differentiation given by this test, it seemed desirable to investigate more fully the possibility of its use, with modifications in procedure, if necessary, in the detection of fungal hyphae in a range of cellulosic fibers, especially cotton and linen. This has been done and the data following have been obtained.

The composition of the stain used was as follows:

Martius Yellow S	0.01 g.
Malachite Green	0.50 g.
Acid Fuchsin	0.10 g.
Distilled water	150 ml.
Ethanol (95%)	50 ml.

The dyes are dissolved together in the ethanol, the water added, and the mixture allowed to stand overnight. The stain has good lasting properties.

The various steps in the staining procedure may be timed, but to get optimum results for each fiber, the time schedule would probably need to be specific for each fiber. To avoid this, each step of the staining procedure can be watched closely and the specimen removed at the critical moment.

The fiber or yarn specimen was thoroughly wetted out in distilled water, and then placed for 15 to 30 sec. in 95% ethanol, more prolonged immersion being avoided as this tends to weaken the depth of color of the subsequent staining. The specimen was then placed in the stain, usually for 1½ to 2 hr., which is adequate for most fibers. For old samples, dyed specimens, or specimens of jute, sisal, or hemp, more satisfactory results were obtained if the staining time was increased to 4 hr. Staining periods longer than those mentioned above do not adversely affect the test, and specimens may be preserved for 2 to 3 months in a bottle of the stain. All excess stain

was then removed by dipping the specimen in distilled water, and this rinsing was continued until it could be seen that the blue color held by the specimen was just beginning to be lost to the water. The specimen was then immersed in 95% ethanol until a blue-green color loss began to occur, the time required for this being short, about 5 to 10 sec. The specimen was then transferred to 95% ethanol acidified with hydrochloric acid to obtain the final color differentiation which the test provides. A concentration of 4 drops of concentrated hydrochloric acid to 30 ml. of ethanol seems satisfactory for flax, but 6 to 10 drops seemed to give better results for the other fibers tested. The specimen was left in the acidified ethanol until the loss of blue color just ceased. The specimen was then placed in 95% ethanol and was removed when the first bit of color began to be lost from the sample. Clearing and mounting of the specimen followed and was accomplished in one of several ways. The clearing may be through a series of three baths, viz., 95% ethanol-benzene 3 to 1, ethanol-benzene 1 to 3, and benzene. The time in the first bath was short, 5 to 10 sec., only until color differentiation could be seen in the specimen. The final bath was longer, 20 to 30 sec. Xylene, toluene, cyclohexane, and cyclohexene may be substituted for benzene. Warm carbol-turpentine may be used as a clearing agent [8] preceded by absolute alcohol rather than 95%. It clears the specimen quickly, and as soon as the differentiation in color is apparent, the specimen should be removed to xylene. For immediate viewing, the fibers may be mounted in a drop of the clearing agent or in α-bromonaphthalene. For more permanent mounting, Canada balsam thinned with the clearing agent may be used. If carbol-turpentine has been used as the clearing agent, a xylene-thinned balsam or cedar-oil makes a satisfactory mounting. These mounts may be preserved for 6 to 12 months, although there may be some fading of the colors if toluene or cyclohexane has been used as the clearing agent. The slide may be viewed under 100 or 200× magnification, at which magnification the hyphae and fibers are clearly distinguished, and good detail of the damage shown. To detect penetrating hyphae, a higher magnification may be necessary.

Although the procedure may at first sight appear somewhat tedious and prolonged, with a little practice the test can be carried through with ease and with dependable results. Further, the difficulties that frequently arise in staining procedures, when counter-staining is required, are not encountered.

Both the Congo Red and the modified Pianese IIIb test described in this paper give a vivid staining of fungal hyphae. However, the latter test, because of the differential staining obtained, provides a considerably more satisfactory degree of contrast since the red color of the hyphae is usually superposed on the green color of the undamaged portions of the cell. This permits a more precise study of the position of the hyphae with reference to the host cell, and this is frequently of importance in judging whether, in the case of cotton, there has been penetration of the lumen by the organism, and in observing the areas in which penetration has occurred. Similarly this advantage of the modified Pianese IIIb test makes it relatively easy to distinguish between superficial growth and deep-seated attack, usually of a cellulolytic character.

III. Application of Modified Pianese IIIb Test

A. *Examination of flax fiber from deteriorated forestry fire hose.* Of the 150 samples returned from the field, a representative total of 42 were examined. Each sample was 12 to 18 in. in length.

The surfaces of the hose showed, in all cases and in varying degrees, a threadbare appearance when examined under the low power microscope. All of the samples showed considerable soiling, some showing, in addition, blackish or brownish discolorations occurring in streaks or irregularly shaped areas. In a few cases, discolored patches of a lighter color were present, the discoloration penetrating through to the inside of the hose. The majority of samples showed one or more fabric breaks, either as ragged holes, slits, or broken yarns, occurring on the flat or along the edges of the samples. Visual examination of the inside of the hose showed an apparently normal appearance with regard to the condition of the yarns, but in the majority of cases the surface carried a brownish discoloration.

Yarns taken from the threadbare areas of the samples appeared to have strong and weak spots as judged by pulling between the fingers. The threadbare appearance of the fabric and the uneven strength of the yarns taken from it are characteristic both of abrasion and microbiological damage.

Samples of new unbleached flax forestry fire hose fabric and samples which had been buried for four weeks resulting in an 85% breaking strength loss

were examined. The new yarn showed an occasional spot of pink or a short pink fiber, but in general, the fibers were uniformly green. The buried sample showed considerable obvious damage, and a large proportion of the fibers were pink. In many instances fungal spores were noted.

The extent of fungus attack in the samples of deteriorated hose was then investigated. Of the 42 samples, 31, or 74%, contained sufficient fungal hyphae to account for severe damage, and 6, or 14%, showed a sufficient amount to indicate moderate damage. In only 5 cases, or 12%, was the amount of hyphal growth small enough to warrant the conclusion that only slight damage had occurred. In these latter two groups, four of the samples showed evidence of chemical damage severe enough to account for the failure of the samples. The failure of the rest of the samples is attributable to mechanical damage, mostly abrasion, in use.

Reference has already been made to the possibility that a cellulosic fiber which has not been subjected to a treatment during manufacture which would destroy the viability of organisms with which it may be contaminated, may, under favorable conditions, undergo microbiological damage at a subsequent stage. In the present instance it was known that the flax yarns used in the manufacture of the hose had received a boil-off treatment. What was not known was whether or not fungal hyphae initially present in the fiber would be removed or altered by the treatment so as to be unrecognizable in the test. Careful examination of the new hose failed to reveal the presence of fungal growth or of damage.

To determine the effect of boiling off, a sample of freshly retted, unboiled flax yarn was subjected to the test. It showed the presence of considerable fungal hyphae and debris on and around the fibers and considerable evidence of damage. A portion of this yarn was boiled off for 1 hr. in 5% sodium carbonate, rinsed well, and then stained. There was no indication of the presence of fungal hyphae or damaged fibers. This may be due to the fact that the hyphae had been removed by the scouring treatment or because the treatment had removed or changed the constituent of the fungal hyphae which gives the characteristic red color in the test.

B. *Examination of cotton.* 1. Undamaged unbleached duck: Yarns raveled from a length of 10-oz. unbleached army duck were subjected to the Pianese IIIb staining procedure. On microscopic examination, the fibers were stained a clear bright green, with some variation in the depth of color. The structure of the fiber was normal. Among the green fibers was found an occasional pink fiber. These green fibers sometimes showed a fine line of reddish color along their edges which appears to be the result of some staining which the cuticle undergoes, but the amount of this was negligible and quite insufficient to alter the over-all green coloring. Likewise, there was some evidence of red coloring at the ends of some of the fibers which possessed a knobbed appearance where the fiber has been separated from the seed.

2. Unbleached cotton exposed outdoors: Determination was made of the incidence of hyphal growth, as judged by the above test, on a sample of unbleached cotton duck which had lost 33% of its breaking strength and undergone a rise in cuprammonium fluidity of 13.1 rhes as the result of exposure outdoors. In cases of this kind, where no fungicide is present, there is usually an appreciable amount of readily visible mildew growth on the underside of the sample, and this was so in the present case.

On applying the differential staining test, specimens of yarn from the sample showed the cotton fibers as uniformly green, without evidence of broken or cracked walls, but with red bodies on the surface of many of the fibers, particularly at the location of the twist. In a few instances there was evidence of hyphal growth within the lumen. In these cases apparently the entry of the organism had been through a cut or broken fiber end, as there was no evidence of surface damage.

In general, therefore, the test indicated that the growth of the fungal organism present was predominantly on the surface of the fiber, with an insignificant amount of damage to the latter. This conclusion was in line with the magnitude of the breaking strength loss and fluidity data.

3. Unbleached cotton subjected to soil burial: The staining test was applied to specimens of yarn taken from a sample of unbleached duck which had been treated with a fungicide of moderate effectiveness and subjected to a four-week standard soil burial test. The sample showed a loss of breaking strength of 80%.

It was found that large numbers of the cotton fibers showed red sections, the color change from green to red usually being abrupt. The red areas

showed severe cracking of the fiber walls, and lateral splitting sometimes extending for the entire visible length of the fiber. There were also a large number of fibers showing ragged and fibrillated ends. Another characteristic feature of a badly damaged fiber was the granular appearance of the interior of the fiber. Some of the green-colored cotton fibers showed evidence of fungal growth on their surfaces, as in the previous case. Where surface damage was severe, there was always some evidence of internal damage.

It has been noted also that as microbiological damage to a fiber progresses, the natural twist is lost. Since it has been observed that damage frequently starts at the point of twist or spiraling of the fiber, and that in an advanced stage of fiber damage there is frequently a regular cracking and splitting of the fiber, it may be that this splitting takes place at the location of the spirals, even though all evidence of spiral twisting has disappeared. This would be in accord with the observation that fibers subjected to severe enzymatic action become fissured along the spirals [2].

The high proportion of obviously damaged fibers, together with the very considerable evidence of the presence of hyphal growth in the fiber lumen, indicated that the high loss in breaking strength suffered by the sample was the result of cellulolytic attack.

4. Effect of presence of dyes: The colors produced by the Pianese IIIb staining test on yarns of bleached and unbleached cotton are very clear and precise, but since it is frequently necessary to examine dyed cotton fabrics, e.g., awnings, for suspected microbiological attack, it was of interest to determine to what extent the presence of dye in the cotton fiber obscured the differential staining in the test.

To study this, the Pianese IIIb test was applied to cotton yarns showing a range of colors in each of several classes of dyes. A summary of the dyes used, and the colors obtained before and after the test, is given in Table III.

It was observed that the colors of the Pianese test, as obtained in undyed fibers, were modified to a greater or lesser extent by the color of the dye in any one class of dye, and also that for any one color, the type of dye had a bearing on the result. But for all dyes and all colors tested there was a sufficiently clear distinction in color between fiber and fungal growth for the test to be quite applicable. Of the colors tested, brown and red seemed to be the

TABLE III. Effect of Presence of Dyes on Colors Obtained in Pianese IIIb Test

Class of dye	Name of dye*	Colors obtained	
		Undamaged	Damaged
Basic	New Methylene Blue AS 1.0%	deep blue-green	bright red-purple
	Safranine TS 0.75%	blue-green	purple
	Brilliant Green Crystals YS	bright blue-green	deep pink-purple
	Bismark Brown A 1.5%	dull apple green	dark purple
	Jute Black 75512	dull green	purple-grey
	Magenta PS	no differentiation	
Sulfur, Thionol colors	Thionol Sky Blue 6 BS 2.0%	blue-green	bright red
	Thionol Brown CL 4, RS 3.0%	dull grey-green	dull red
	Thionol Brilliant Green GS 5.0%	dark green	red
	Thionol Brown 4 RS (copper chrome) 15%	green with very reddish brown cast	rust
	Liquid Thionol Black RS 20%	green-black	red
Direct, Chlorazol colors	Chlorazol Sky Blue GWS 1.25%	grey-green	purple
	Chlorazol Fast Scarlet GS 1.5%	grey-green to green	purple
	Chlorazol Green BNS 3.0%	dull dark green	slate or grey-purple
	CR Nigger Chlorazol Brown N 2.0%	muddy green	brick
	Chlorazol Black ES 5.0%	blue-green	pinkish or grey-purple
Vat Caledon colors	Caledon Blue RCS paste 10%	pale blue-green	purple
	Caledon Red FFS paste 10%	dull grey-green	purple
	Caledon Jade Green GS paste 10%	dull pale green	red
	Caledon Brown GS paste 10%	greyish or brownish green	red-purple

* All of the dyes were products of Imperial Chemical Industries, Manchester, England.

most difficult to obscure. Of the classes of dyes, the basic dyes have the least effect in distorting the normal colors of the test, and the thionol dyes, the greatest. The Chlorozol-dyed yarns give somewhat better results than the vat-dyed.

5. The effect of cotton fiber maturity: The presence of an occasional pink fiber among the green of an undamaged sample, which, in spite of its color, gave no indication of damage, suggested the possibility that part of the red color in a slide of damaged fibers stained by this test, might be due to other than a microbiological effect. These possibilities include such effects as fiber maturity, and the claim that a stain may color mature and immature fibers differently has been made by a number of workers. For example, the stain employed by Goldthwait and his co-workers [14, 15] is claimed to stain mature fibers red and immature fibers green.

The detection of degree of fiber maturity is a subject which is outside the scope of the main investigation covered in this paper, but it was considered to be of interest to determine whether the Pianese IIIb technique was of value in this connection. Samples of stated degrees of maturity were therefore obtained and tested.

It was found that in samples of a low degree of maturity (40%) there was a large number of fibers which did not show the typical green color of the undamaged mature fiber. The color of these fibers ranged from practically colorless to pale pink, to pink; some of the fibers were straw-colored. As the degree of maturity of the samples increased from 40 to 75 to 90%, the proportion of pink to green fibers decreased rapidly. In general, these pink fibers showed the normal structure of a cotton fiber, except that the walls were thinner, and on the whole, the fibers appeared somewhat narrower, with more twists in a given length; but there was no difficulty in distinguishing the undamaged pink fibers referred to above from red mature fibers which had been subjected to microbiological attack. Except for their red color, immature fibers are identical in appearance to undamaged mature fibers (with the possible exceptions above mentioned). Where immature fibers have been microbiologically damaged, the same deep-red coloration appears as in mature damaged fibers, but the background color is pink instead of green. However, where the damage was severe enough for the entire fiber to take on the red coloration, no distinction could be drawn between mature and immature fibers.

6. Examination of "cavitomic" cottons [16, 35]: Samples of cotton from a number of bales of so-called cavitomic cotton were examined, portions of each sample being stained according to the Pianese IIIb method. On examination, the slides showed the presence of both immature and mature fibers, both damaged and undamaged. Although surface damage was found, internal or cellulolytic-type damage predominated.

7. Examination of damage of uncertain origin: As mentioned earlier, microbiological damage can occur with little visual evidence. As a case in point, a badly damaged cotton shower curtain containing a vat green dye, which was being tested to determine the cause of damage was subjected to the Pianese IIIb test. The yarns were weak enough to be broken at any point with the fingers, and in places the curtain was shredded. There was practically no indication of mildew, except for a few small isolated spots of thinly scattered growth. It was believed that the damage was probably chemical, possibly resulting from a combination of alternate wetting and drying and vat dye damage. Yarns were taken from a number of places, a duplicate specimen from each location being used for the fluidity test, and subjected to the Pianese test. It was found that in each of the slides well over 75% of the fibers were severely tendered by microbiological attack. The increase in fluidity over the normal was negligible.

C. *Examination of viscose rayon.* The Pianese IIIb stain produced the typical green color of the test in undamaged viscose filaments. The longitudinal striations were clearly visible and the filament was not distorted in any way. To obtain microbial damage, some of the material was buried for five days, and then stained and examined. Red granular surface deposits were observed as well as interior damage, as indicated by the red coloration, with some breakdown of some filaments. The results with delustered viscose were similar.

D. *Examination of sisal.* Lengths of sisal cordage, new and after undergoing soil burial, were untwisted and the yarns stained. The sisal "fiber" consists of a large number of stiff, thick-walled cells or fibers, interlaced with spiral vessels and parenchymatous cells, and held together by bonding materials. On staining, this composite fiber took on a deep blue-green color, and the nonfibrous material (for example spiral vessels), a purple color. In the buried sample, there was some surface damage of a reddish color, readily distinguishable from the purple

spiral vessels by reason both of the color and form. On teasing out the individual fibers, the blue-green color of the undamaged fibers was clearly seen. Damaged fibers stained a pale purplish red.

Early internal damage appeared somewhat granular in character, but in a more severely damaged fiber this granular appearance was largely lost, the fiber being a uniformly pale reddish purple. Even in cases of severe damage, the characteristic cylindrical appearance of the individual fiber is not completely lost.

E. *Examination of jute.* The source of material was lengths of new and buried jute hessian. Like sisal, the jute fiber is a composite fiber. On staining, it appeared a deep green, and surface damage on the fiber was red in color. When the individual fibers were separated out, the green color of the undamaged fiber was clearly seen, and damaged fibers were stained red.

F. *Examination of hemp.* Lengths of new and buried Italian hemp cordage were used. The fiber was stained green with Pianese IIIb stain, with the transverse joints a darker green. Damaged areas stained a purple-red. The fiber consists of a number of cells, and on teasing out the individual fibers, the damaged ones showed the purple-red color either in areas throughout the green or throughout the entire length of the cell.

IV. Attempts to Assess Degree of Damage with the Pianese IIIb Stain

Several attempts were made to establish a method by which levels of microbiological damage, as shown by this test, could be measured on cotton.

In the first place, yarns were taken from a sample of cotton fabric and damaged by microbiological attack to a known degree, as measured by breaking strength loss. They were cut into 1-mm. lengths, stained, and several slides made from them. The red and green fibers were counted. It was hoped that for different degrees of damage, a definite ratio of red to green fibers could be established, but so great was the variation between slides and also the difficulty in classifying some of the fibers, that a reliable ratio was impossible, even when large numbers of fibers were examined. In view of this large variation, it would be impossible to distinguish between samples with relatively small differences in damage.

Next, yarns from samples of known degrees of damage were stained, put through the Wiley mill, and pads made. Attempts were made to measure, with a photometer, the quantity of the green and red components of the pads. But it was found that all the pads gave similar readings, even though the range of damage of the samples from which the pads were made, was known to be extensive. It is believed that this difficulty is related to the manner in which a cotton fiber undergoes microbiological attack. Throughout all of its stages such attack is highly localized and results in the almost complete disintegration of relatively small sections of the fiber. Even where the attack has been severe, the proportion of fiber thus disintegrated is not large, although, because the disintegration has led to a drastic reduction in mean fiber length, the breaking strength of the yarn or fabric will have been greatly reduced. This effect, together with some loss, in the Wiley mill, of disintegrated material containing the fungal hyphae, would serve to explain the fact that the over-all color of the surviving fibers is not very different for widely varying degrees of attack, as measured by breaking strength loss. That the loss of material in the Wiley mill was not a major factor was shown by staining swatches of fabric which had been degraded to varying degrees by microbiological action. It was found that these, also, did not show a well-marked gradation of color from green to red.

Conclusions

It has been shown that the Pianese IIIb differential staining technique is a useful method for detecting the presence of fungal hyphae in or on certain cellulosic fibers which have been damaged microbiologically. The method is readily applicable to cotton, flax, viscose, jute, sisal, and hemp fibers. The presence of dyes in the fibers does not appreciably affect the test.

The Pianese IIIb staining procedure does not demonstrate other kinds of damage, e.g., acid or mechanical, but is specific for microbiological damage. The stain causes a minimal swelling of the fibers, and therefore the structure of the fiber is not destroyed by the stain, thus preventing any accentuation of damage present.

The test may be of use in determining the degree of maturity of cotton fibers, and in addition, provide some indication of the extent of damage that may have taken place in raw cotton.

The procedure is believed to be a valuable tool in detecting the presence of fungal damage in cellulosic fibers subjected to fungal contamination during the latter stages of their growth or during harvesting, as in the case of cotton, or in fiber separation processes involving microbiological action, as in the retting of flax.

It is believed that the test can serve as a useful additional routine, preliminary test in determining the cause of damage in a sample where the source of damage is unknown. With a little practice, it can be carried out with relative speed and ease.

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A New Cotton Lustermeter for Yarns and Fibers[1]

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Abstract

A single-answer, direct-reading instrument especially adapted for measuring luster of raw cotton and grey and mercerized yarns has been developed. It includes a special sample clamp, and a turret-top holder for the instrument. The sample is illuminated at 45° and measured at 0° and 45°. By means of a special circuit, the ratio of these two measurements may be read directly from an automatically indicating scale in terms of "per cent luster." Samples are easily and quickly prepared from yarn skeins on special holders, and a similar but narrower holder is used for measuring combed fibers from pinches of blended raw stock samples. Results are related to goniophotometric measurements made for several conditions of illumination. Luster, sample preparation and holder, the instrument, calibration, and luster results for the USDA's Standardized Variety Series of cottons are discussed and summarized. The instrument is an adaptation of a simplified all-purpose glossmeter under development by R. S. Hunter.

THERE is much current interest in luster of cotton textiles and in the possibilities of increasing luster by any one of a number of methods. Ransom and Edelstein [8] reported in 1937 on luster determinations of cotton, and Fourt [2] and his associates at the Harris Laboratories have published in *Textile Research Journal* in recent years a series of reports on "Improvements of Luster in Cotton." There has been other work on luster of cotton, some of it at the Shirley Institute as early as 1923–1925. Buck [1], in 1949, reported on the market demand for luster in cotton and summarized the technical background of the subject, particularly as it concerns cotton in fibers, yarns, and textiles. Recent studies by Jeffries [7] report on delustering of filament fabrics, and discuss the reflection of unpolarized light and of plane-polarized light in relation to the effect of delustering. On the more general subject of gloss and luster there are reports by Hunter [4, 5, 6] beginning in 1937, and in 1949 a critical study was made by Harrison [3] of the extensive literature on the subject in which he assesses the present state of our knowledge on gloss.

When it became advisable recently for our laboratories to consider making routine luster measurements, we consulted Richard S. Hunter of Hunter Associates in Falls Church, Va., who has had close association with gloss problems at the National Bureau of Standards, and later with problems of gloss instrumentation at the Gardner Laboratories. We went to him with the problem of developing a single-answer, direct-reading instrument and a new and rapid method of sample preparation and measurement that would be based on preliminary ideas worked out in our own laboratories. He was already far enough along on a new design for a simplified all-purpose gloss instrument to be able to supply us at once with a model for trial use, one which later was modified to meet our special needs. But before discussing instrumentation, it may be well to point out what it is that we wish to measure.

Luster

Luster may be defined as the appearance of a surface which results from its power to exhibit mirrorlike reflections. It is for textiles what gloss is to the ceramist or to the paper maker. Hunter, in 1937, called attention to six types of gloss, each with a different appearance criterion, and each of which is measured, if measured at all, in a different way. These are listed and described in Table I.

From this table we find that contrast gloss (the contrast between specularly reflecting areas and other areas in a sample) seems most applicable to tests of

[1] Based on the paper given at the National Cotton Council's Cotton Research Clinic, Pinehurst, N.C., February 15–17, 1956.

TABLE I. Hunter's Tabulation of Six Appearance Criteria for Gloss

Type of Gloss	Perceptual (Appearance) Criterion	Reflectance Function	Classes of Surfaces Involved
Specular gloss.....	Shininess, brilliance of highlights	I S; $G_s \sim S/I$	Medium-gloss surfaces of paint, plastics, etc.
Sheen.....	Shininess at grazing angles	I Sh; $G_{sh} \sim Sh/I$	Low-gloss surfaces of paint, paper, etc.
Contrast gloss.....	Contrast between specularly reflecting areas and other areas	I D S; $G_c \sim S/D$	Low-gloss surfaces of paint, textile cloth, etc.
Absence-of-bloom-gloss.....	Absence of haze, or milky appearance adjacent to reflected highlights	I D B; $G_b \sim (B-D)/I$	High- and semigloss surfaces in which reflected highlights may be seen
Distinctness-of-image gloss.....	The distinctness and sharpness of mirror images	Not yet measured as function of reflectance	High-gloss surfaces in which mirror images may be seen
Surface-uniformity gloss.....	Surface uniformity, freedom from visible nonuniformities	Not function of reflectance	Medium-to-high-gloss surfaces of all types

textile luster since this is the method that seems to parallel most closely our visual method of judging luster. While it is usual to express contrast gloss as a ratio, the difference between the dark and highlight areas might also be used as a measure.

As Buck points out, luster is very complex, it involves physical, physiological, and psychophysical considerations. One consequence is that the scales resulting from different instruments and methods of measurement are on quite different levels. This is indicated in Figure 1, adapted from a diagram by R. S. Hunter, in which the scale of measurement for the new cotton instrument is shown in comparison to scale levels representing qualitative differences between scales of a number of well-known gloss-measuring methods and instruments.

The index of contrast gloss has been expressed by Hunter [5] and Fourt [2] as the ratio of the specular reflectance to the diffuse reflectance components, S/D. This means that when the reflectance of the diffuse and specular components are the same, the ratio is 1.0, or zero gloss. At the top limit for mercerized Pima cotton yarns, the reflectance (specular) at 45° may be about 2.5 times the reflectance at 0° (diffuse). While S/D ratios (which range for cottons from 1.0 for zero gloss to 2.5 for high gloss) provide a scale satisfactory for those working in the laboratory, a scale in terms of per cent gloss seems easier to interpret by those not familiar with the instrument. Such a scale has been provided for the new instrument, using the same photoelectric signals

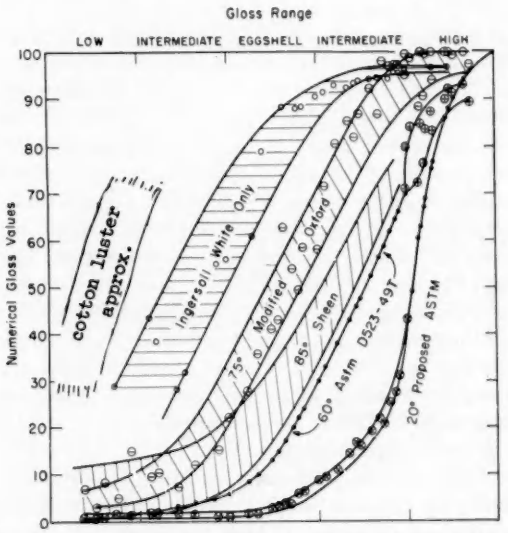

Fig. 1. Scale of new Cotton Lustermeter shown in comparison to scale levels of a number of well-known gloss-measuring methods and instruments. (Adapted from figure 12, R. S. Hunter, *ASTM Bull.* 186, Dec. 1952.)

TABLE II. Equivalents for Two Scales of Gloss Contrast (G_c)

G_c (% luster) $100\,[1-(D/S)]$	G_c (index) S/D
0	1.00
10	1.10
20	1.25
30	1.43
40	1.67
50	2.00
60	2.50
70	3.33
80	5.00
90	10.00
100	∝

(reflectances at 0° and 45°), but reading them as $1-(D/S)$, or its equivalent $(S-D)/S$. When multiplied by 100, this provides a scale in which zero luster is represented by 0, and the highest gloss by 100. On this scale cotton fibers held flat and parallel in clamps measure about 60 to 70% luster, grey [2] cotton yarns similarly held measure about 30 to 40% luster, and mercerized yarns about 40 to 50% luster. In 1951 a D-13 committee used this scale and found that on it dull rayons measured about 45–65, and bright rayons 95–98.

Table II provides a conversion table for the two scales, per cent luster as read from the new Cotton Lustermeter, and the "Index of Luster" used by Fourt and others. In both scales the low end is much expanded. This suits the purpose of measuring cottons, but it is important to remember that neither scale is an equi-sense scale in which a unit of scale difference indicates an equal sensory difference in luster.

The usual method for lighting and viewing textiles has been to adopt 45° illumination, with 0° for diffuse viewing, and 45° for specular viewing. While this practice has been followed in the Cotton Lustermeter, it was believed that more information should be available before luster measurements of cotton were frozen by custom to these specifications. Therefore, in checking the level of results to be expected for cotton yarns under different illuminating and viewing conditions, a limited study was made of reflectances at various angles of illuminating and viewing on a selected number of cotton yarn samples. These results, in the form of goniophotometric curves made on the Hunter Automatic Recording Goniophotometer, are shown in Figures 2 to 4.

In order to place the results on cotton in proper perspective, attention is first called to the very considerable difference between the reflectance gradient for cottons and for materials more usually considered to be glossy. Gradients that differ by 100 to 1 for reflectances measured at 0° and 45° angles are not uncommon. On the left side of Figure 2, goniophotometric curves are shown for a few typical paper samples.[3] As this diagram indicates, the 0°–45° ratio is high for all but one curve. On the right of this figure, curves are plotted for a number of 50/1 yarns, each yarn made from a different variety of cotton. Ratios of the 0°–45° reflectances for these yarns are all less than 2 to 1. From this demonstration it should be clear how much the luster of cards of parallel cotton yarns differs from that of surfaces more usually thought of as glossy or lustrous.

In order to get better precision for reading the curves in the cotton luster range, the circuitry of the goniophotometer was adjusted to increase sensitivity, and the curves that follow were made with this circuitry on an expanded scale.

Goniophotometric curves for a pair of Acala and a pair of Pima 50/1 yarns under three different angles of illumination are shown in Figure 3. In the top pair of diagrams these yarns are illuminated at 45° and measured through angles of view from +10° to −75°. In the middle diagrams these same yarns are illuminated at 60° and viewed from +30° through to −70°. In the bottom diagrams they are illuminated at 75° and viewed from +40 through −75°.

While the increased angle of illumination in these curves provides a higher contrast ratio, as shown in Table III, the variability between samples is also increased, and the use of greater angles crowds the level of results at the high end of the scale. Since the scale levels that result from the 0°/45° conditions provide differentiation that agrees adequately with results of observation on cotton yarns, and since the 45° specular angle has been used for most previous studies, it was decided that these conditions should be made standard for the new Cotton Lustermeter.

To illustrate the differences in measured luster

[2] Grey (or "greige") is a commonly used textile term applied to yarns or fabrics in the unfinished state and does not refer to the color of the material.

[3] Adapted from Figure 2, R. S. Hunter, *TAPPI* **38**, 19 (Jan. 1955).

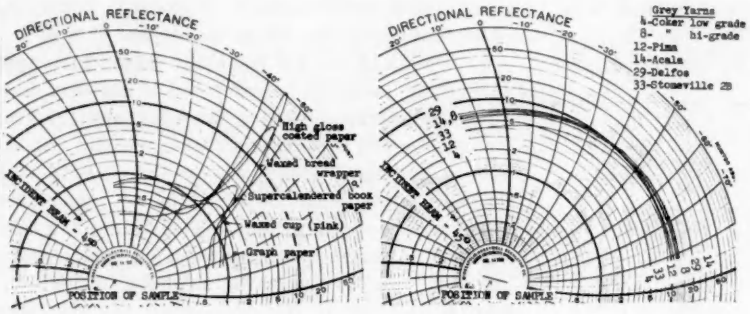

Fig. 2. Diagrams illustrating reflectance gradients for paper (at left) which may differ by 100 to 1 at 0° and 45° compared to those for cotton (at right) in which the gradients are nearer to 2 to 1 for reflectances at 0° and 45°. (Goniophotometric data for paper, courtesy R. S. Hunter.)

TABLE III. Per Cent Luster, as Calculated for Contrast Ratio $1-(D/S)$ for Pairs of Acala and Pima 50/1 Cotton Yarns, Grey and Mercerized

Ident.	% Luster Ill. at 45° $D=0°, S=45°$	Ill. at 60° $D=0°, S=60°$	Ill. at 75° $D=0°, S=75°$
Acala			
Grey	34	46	78
Merc.	44	63	84
Pima			
Grey	39	61	83
Merc.	50	71	89

TABLE IV. Per Cent Luster $1-(D/S)$ for Pairs of Acala and Pima Cotton Yarns, Grey and Mercerized, for Different Counts and Ply, Illumination at 45°

Sample identification	% Luster for specified yarn counts and ply 22/1	50/1	23/2
Acala			
Grey	34	33	47
Merc.	44	41	59
Pima			
Grey	39	39	48
Merc.	50	50	70

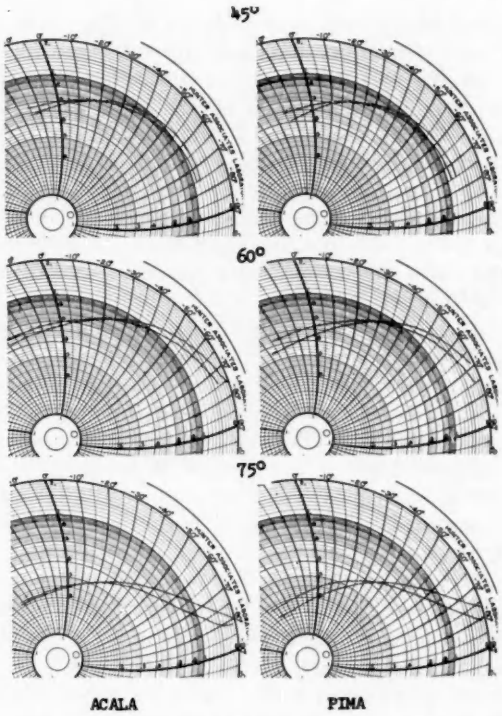

Fig. 3. Goniophotometric curves for two pair of 50/1 yarns, grey and mercerized, under three angles of illumination: 45°, 60°, and 75°.

that may be introduced by yarn size and yarn ply, goniophotometric curves are shown in Figure 4 for pairs of grey and mercerized Acala and Pima cotton yarns: 50/1, 22/1, and 23/2. These are illuminated at 45°. As shown in Table IV, the luster level changes very little between 50/1 and 22/1 yarns, but plying the yarns increases the measured luster considerably, as shown by the 23/2 yarns.

Differences in reflectance levels of high- and low-grade cottons are illustrated in Figure 5. Sample 1 is a yarn made from high-grade cotton, and samples 2 and 3 from low-grade cottons. From Table V,

TABLE V. Per Cent Luster by Contrast (G_c) and by Difference (G_s) for Yarns Made from High- and Low-Grade (High- and Low-Reflectance) Cottons, to Illustrate Effect of Color on Luster Measurements

Sample identification	Directional reflectance		Gloss values	
	$D = R_d$ (45°, 0°)	$S = R_d$ (45°, 45°)	$G_c = 1 - (D/S)$	$G_s = S - D$
No. 1 Coker, high grade	0.62	0.91	0.32	0.29
No. 2 Coker, low grade	0.43	0.68	0.37	0.25
No. 3 DPL, low grade	0.45	0.70	0.36	0.25

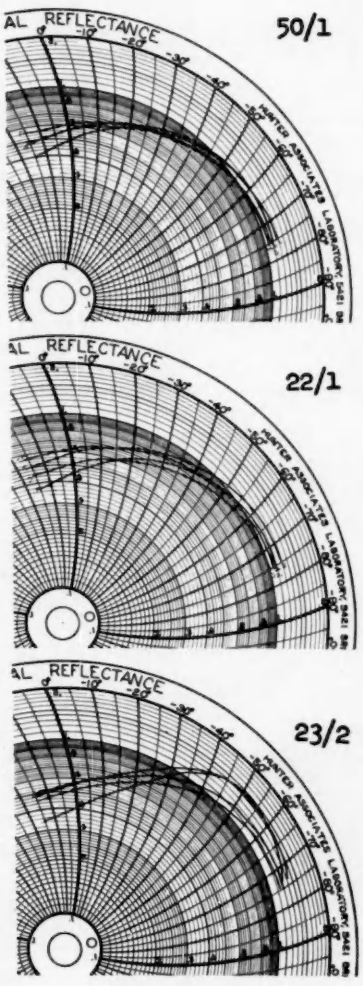

Fig. 4. Goniophotometric curves for pairs of Acala and Pima grey and mercerized yarns, illuminated at 45°, in different yarn form: 50/1, 22/1, and 23/2.

based on values of directional reflectance for 45° incident light, it is evident that although the increase in reflectance from 0° to 45° viewing is greater for the high-grade (high-reflectance) sample, the contrast gloss values are higher for the low-grade (low-reflectance) samples.

The dark color (low reflectance) of the low-grade samples is what makes the computed contrast-gloss values higher for them than for the high-grade sample. While the reflectance differences between these high- and low-grade samples are extreme, and usual differences would be considerably smaller, nevertheless one should keep in mind the fact that the level of reflectance associated with the color of the sample may need to be known when one interprets luster differences that are expressed in terms of a contrast ratio.

Perhaps it may help the reader to understand this anomaly by referring to an outstanding example of a large difference of this kind, that is, the relative glossiness of polished black and white glasses. The specular reflectance, as seen in the highlights, might be nearly the same for a black and a white glass, but

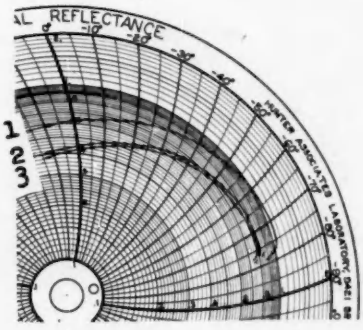

Fig. 5. Goniophotometric curves of yarns made from high (1) and low grade (2, 3) cottons.

the diffuse reflectance (at 0°) for the black would be near zero and for the white near 100%. This would give a gloss-contrast ratio higher for the black sample than for the white. In this case one probably would agree that the higher gloss measurement for the black glass is in agreement with a visual assessment of the gloss of these two samples. For differences in yarn samples made from cottons similar in all respects except grade, it is not so clearly evident that samples made from the lower grades would appear more lustrous. The experimental work necessary to establish scales of uniform sensory differences for low-contrast gloss has not yet been done, and without information of this nature we are not at the present time in a position to do more than call attention to this possible source of discrepancy when one compares luster data for samples that are not in the same general level of color.

Physical measurements of gloss are provided by goniophotometric curves, such as those illustrated in Figures 2 to 5. They provide the basic information to which all short-cut methods should be related, and are needed as a basis upon which to decide upon conditions to be used in building an instrument, and for calibrating an instrument after it is built. The data in Table VI, taken from the originals of

TABLE VI. Goniophotometric Data on Cotton Yarns Read from Curves Made on Hunter's Automatic Recording Goniophotometer Using a 2 to 1 Scale *

Curve sheet	Sample description					Angle of view, deg.												
	No.	Variety	Grade	Yarn size	Cond.	−40	−30	−20	−10	0	10	20	30	40	45	50	60	70	75
						Reflectance for 45° illumination													
1	1	Coker	High	22/1	Grey				0.58	0.62	0.68	0.74	0.80	0.87	0.91	0.95	1.01	1.05	
	2	Coker	Low	22/1	Grey				0.40	0.43	0.48	0.52	0.58	0.64	0.68	0.70	0.76	0.80	
	3	DPL	Low	22/1	Grey				0.42	0.45	0.50	0.54	0.60	0.67	0.70	0.72	0.78	0.82	
2	4	Acala		23/2	Grey				0.51	0.57	0.64	0.74	0.88	1.02	1.08	1.12	1.28	1.29	
	5	Acala		23/2	Merc.				0.50	0.56	0.65	0.79	1.01	1.28	1.38	1.45	1.46	1.39	
	6	Pima		23/2	Grey				0.47	0.52	0.58	0.68	0.80	0.94	1.00	1.05	1.12	1.14	
	7	Pima		23/2	Merc.				0.36	0.41	0.50	0.65	0.91	1.20	1.37	1.44	1.40	1.28	
3	15	Acala		22/1	Grey				0.58	0.62	0.68	0.75	0.82	0.89	0.93	0.97	1.02	1.07	
	16	Acala		22/1	Merc.				0.54	0.59	0.67	0.76	0.86	0.95	1.00	1.04	1.12	1.18	
	17	Pima		22/1	Grey				0.47	0.51	0.57	0.64	0.70	0.79	0.84	0.88	0.96	1.00	
	18	Pima		22/1	Merc.				0.39	0.46	0.55	0.66	0.76	0.86	0.92	0.97	1.04	1.08	
4	8	Acala		50/1	Grey				0.58	0.63	0.70	0.78	0.87	0.98	1.02	1.06	1.12	1.18	
	10	Pima		50/1	Grey				0.54	0.59	0.66	0.72	0.81	0.89	0.94	0.99	1.05	1.10	
	12	Delfos		50/1	Grey				0.58	0.63	0.68	0.74	0.81	0.89	0.92	0.96	1.02	1.06	
	13	Stoneville 2B		50/1	Grey				0.54	0.57	0.61	0.67	0.73	0.80	0.84	0.87	0.95	1.00	
	14	Coker	High	50/1	Grey				0.58	0.63	0.68	0.74	0.81	0.89	0.92	0.96	1.02	1.06	
5	8	Acala		50/1	Grey				0.57	0.61	0.67	0.73	0.80	0.88	0.92	0.96	1.02	1.06	
	9	Acala		50/1	Merc.				0.50	0.56	0.64	0.74	0.84	0.95	1.00	1.04	1.10	1.14	
6	10	Pima		50/1	Grey				0.50	0.56	0.62	0.70	0.78	0.86	0.91	0.95	1.03	1.08	
	11	Pima		50/1	Merc.				0.42	0.50	0.59	0.70	0.80	0.92	0.99	1.04	1.11	1.19	
7	8	Acala		50/1	Grey				0.56	0.60	0.66	0.72	0.79	0.86	0.90	0.94	1.02	1.05	
	9	Acala		50/1	Merc.				0.50	0.56	0.64	0.73	0.82	0.94	0.98	1.02	1.10	1.13	
	10	Pima		50/1	Grey				0.49	0.55	0.60	0.68	0.76	0.84	0.88	0.92	1.02	1.05	
	11	Pima		50/1	Merc.				0.42	0.49	0.59	0.70	0.80	0.92	0.98	1.02	1.10	1.13	
						Reflectance for 60° illumination													
8	8	Acala		50/1	Grey			0.51	0.53	0.56	0.60	0.66	0.75	0.86	0.98		1.12	1.30	1.53
	9	Acala		50/1	Merc.			0.45	0.47	0.50	0.56	0.63	0.75	0.90	1.06		1.27	1.50	1.75
9	10	Pima		50/1	Grey			0.44	0.46	0.49	0.54	0.62	0.72	0.84	1.00		1.18	1.40	1.30
	11	Pima		50/1	Merc.			0.36	0.37	0.40	0.46	0.54	0.68	0.77	1.08		1.32	1.60	1.92
						Reflectance for 75° illumination													
10	8	Acala		50/1	Grey	0.22	0.22	0.23	0.24	0.26	0.28	0.32	0.37	0.44		0.52	0.65	0.90	1.12
	9	Acala		50/1	Merc.	0.21	0.21	0.21	0.23	0.25	0.28	0.32	0.38	0.47		0.60	0.80	1.17	1.50
11	10	Pima		50/1	Grey	0.19	0.20	0.21	0.22	0.25	0.28	0.33	0.39	0.47		0.59	0.76	1.08	1.40
	11	Pima		50/1	Merc.	0.16	0.16	0.17	0.18	0.20	0.24	0.29	0.37	0.48		0.55	0.92	1.38	1.84

* On this scale 1.0 is the reflectance for a diffuse white.

the curves in Figures 2 to 5, have been so used in building and calibrating our Cotton Lustermeter. They are given in detail for convenience of others working with the basic problem of cotton luster.

Sample Preparation and Holder

An important problem in developing the Cotton Lustermeter was to reduce the amount of work in preparing samples for measurement. Since yarns usually can be made easily available in skein form, a stand was built something like a skein holder with a movable bar at the top (movable so that the skeins could be doubled or used full length). A hook fastened at the end of a spring, is attached to this bar. At the bottom of the stand there is a milled slot to hold the sample clamp during loading. This stand, with sample clamp in place and loaded with yarn, is illustrated in Figure 6. Details of the sample clamp are shown in Figure 7: the one at the left for yarns, the one at the right for fibers. The sample clamp for yarn has a $\frac{3}{4}$ in. wide guide groove for the skein on the underside (upper side in Figure 7), and a $\frac{1}{64}$-in. groove at the sides to absorb the skein bulk. It has a tongue $1\frac{1}{4}$ in. wide. Since we wished to measure samples of raw cotton as well as yarns, a similar holder was built with a $\frac{1}{2}$-in. tongue to allow for measurement of cottons as short as $\frac{7}{8}$-in. staple.

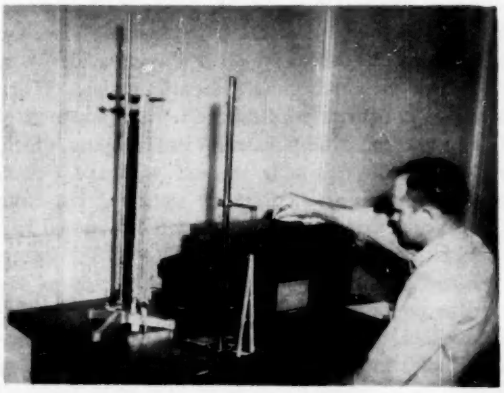

Fig. 6. Cotton Lustermeter, with automatic indicator in center front and turret-top holder in place, shown in operation. Shown also is the stand for holding the yarn for loading into the sample clamp.

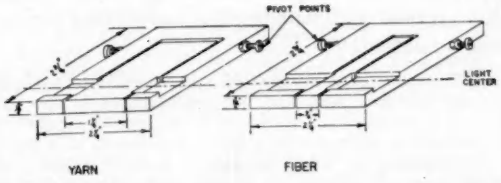

Fig. 7. Details of sample clamp. For yarns the tongue is $1\frac{1}{4}$" wide, for fibers it is reduced to $\frac{1}{2}$" in order to accommodate short staple cottons.

After removal from the loading slot, the loaded sample clamp is ready to place on the instrument in the special turret-top device which the operator in Figure 6 is adjusting. This device allows a 180° turn of the sample so that it can be measured along its parallel axis, first from one direction, then the other. Non-uniformity in sample preparation will show up by differences in these two measurements.

With a skein length sufficient to provide a consistent bulk in the holder (the equivalent of about 240 yd. of 22/1 yarn, 120 yd. of 22/2 yarn, or 480 yd. of 50/1 yarn), the operator slips the skein sample over the hook of the loading stand and under the $\frac{3}{4}$-in. grooved guides of the sample clamp, keeping as parallel as possible the threads of that part of the sample that is placed under the holder. Then with a machine screw used as a comb he gently combs over the skein a very few times to make the threads more parallel than is possible by hand alone. After the threads are reasonably flat and parallel, the tongue of the clamp is brought up under these paralleled threads and pushed gently up into place until the top of the tongue is even with the top of the clamp, even, but no more, or the sample will pillow and will not go into the turret holder with the threads flat and parallel.

When an operator prepares to measure a combed sample of raw stock fibers, he uses a clamp with the $\frac{1}{2}$-in. tongue, and places the sample on the top (instead of the bottom) of the clamp. He holds the fibers taut with a fiber clamp or with fingers of one hand and the thumb of the other, using the remaining fingers of the other hand to push the tongue of the holder down on the paralleled fibers until they are held in place by pressure of the tongue against the sides of the holder. In the clamp used with fibers, it is not necessary to provide grooves on the inside since the fiber sample is not bulky enough to require it.

The Instrument

Usually one would describe an instrument before a sample holder. But in this case it was very impor-

tant to know just what kind and size of sample would be required, and the size of the sample holder, before the instrument itself could be completed. In order to allow for measurements of short as well as long staple fibers, the instrument was set up on the basis of measuring a sample ½ in. long, and this led to the requirement of a ½-in. square sample. Sensitivity requirements for measuring this size sample were then built into the instrument.

The resulting instrument, Hunterlab Cotton Lustermeter Model D16C, with automatic indicator in the center front, and with turret-top sample holder in place, is shown in Figure 6.

Figure 8 shows the interior of the instrument, with the position of the lamp at 45° to the sample, one phototube directly under the sample to receive light diffusely at 0° angle, and the second at +45°, to receive specular light. A switch with three positions, and a third phototube monitoring the lamp directly, make possible direct readings on the per cent luster scale already described, and separate readings of diffuse and specular reflectance. Each of the three scales, specular reflectance at 45° (S), diffuse reflectance at 0° (D), and the single number scale based on the formula: Per cent luster = $100[1 - (D/S)]$, has a separate calibrating knob, provided so that readings may be taken directly from the single three-place digital dial.

Basically the Cotton Lustermeter is an early model of a new, simplified, all-purpose gloss instrument that Hunter has near completion at the present time. The instrument is sturdy and serviceable for use in a testing laboratory. Phototubes (1P39) are used as the detecting devices because of their excellent stability and good performance in the Wheatstone bridge type of measuring circuit that is employed. Tubes must be selected carefully both for initial use and for replacement if measurements are to be accurate and reproducible from one instrument to another. Spectral sensitivity of these tubes is known to be variable from one to another, and it has been found that they vary also with angle of view. In the present cotton instrument, tubes must be selected, but a method of overcoming this difficulty has been found that can be used on later models.

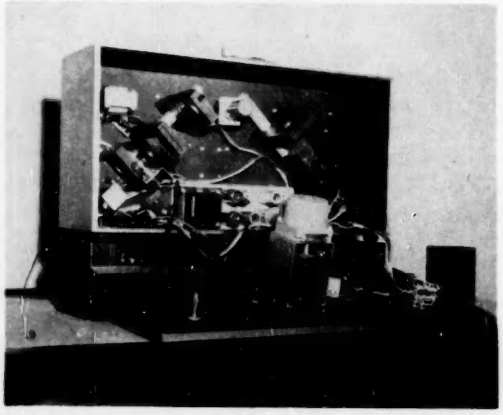

Fig. 8. Interior of Cotton Lustermeter. See text for explanation.

Calibration

No instrument is better than its calibration, and for calibration one needs standards suitable for use on his own instrument. The National Bureau of Standards puts out 4 × 4-in. plaques for gloss measurements by certain ASTM methods, but none of these seemed adequate for use with the low-luster cotton instrument. It is difficult to obtain low-gloss standards. Hunter supplied a wallboard sample with near zero contrast gloss at usual angles of illumination, but obviously that had too perishable a surface for use as a standard. At NBS low-gloss tiles were tried from their 60° gloss standards series. When these did not prove successful, H. K. Hammond of NBS suggested a de-polished Vitrolite glass which, on trial, seemed suitable for use with the Cotton Lustermeter. Two-inch square samples,[4] cut from a 4-in. panel and photometered at the National Bureau of Standards, measured 13.1 to 13.3% luster. Measured on the Hunter Goniophotometer at the time the cotton yarns were measured, the matt surface wallboard measured −1.5, and one of the Vitrolite samples measured 14.1. Different placement of samples, and different sample areas may be involved in these measurements, and a still different area (½ in. square) is used in standardizing the instrument. Because of these several possible sources of difference, it was decided that the agreement seemed adequate, and the Vitrolite glass was adopted for use as our standard.

[4] While the angular aperture of light in the beam needs to be more narrowly controlled for measurements of specular than for contrast gloss, nevertheless "to describe completely the reflectance indication of a given glossmeter, it is practically necessary to have a drawing to scale of its complete optical system." (From [4], p. 28.) The sample used in calibration, and the geometry of the instrument on which its gloss is measured, have a direct bearing on the results obtained.

Measurements in Table VII are given for direct readings on the Cotton Lustermeter, using this Vitrolite standard, and for readings on the same yarns as they are calculated from goniophotometric data. Color measurements, made of the identical samples measured on the Cotton Lustermeter, are reported in terms of the reflectance (R_d) and yellowness ($+b$) scales of the Gardner Automatic Color Difference Meter now in routine use at our Clemson laboratories. From this table it can be seen that for most yarns the luster measurements agree very well by the two methods, particularly when it is considered that only one measurement was made on each instrument, and a different sample was prepared for each. Note that the reflectance measurements for color are well above the measurements at 0° and far below those at 45°. This results from the fact that the diffuse reflectance pickup of the Color Difference Meter includes a wide cone of angles centering about 0°.

Use of Instrument

The instrument was first tried out in the spring of 1955 on several hundred samples of yarns used in a pilot finishing test study. This was with a barrier layer cell detector, and with separate S and D scales. During the summer the instrument was revised, phototubes installed, and the scale made direct-read-

TABLE VII. Color and Comparative Luster Data on a Selected Series of 18 Cotton Yarns. Luster Measurements Are as Read Directly from the Cotton Lustermeter, and as Calculated from Goniophotometric Measurements

Sample identification				Color		Luster, illumination incident at 45° from					
						Lustermeter	Goniophotometer				
						$\frac{S-D}{S}$	D	S	$S-D$	$\frac{S-D}{S}$	$\frac{S}{D}$
Cotton	Yarn size and No.	Cond.	No.	R_d	$+b$	G_c	R_0*	R_{45}*	G_s	G_c	G_c
Acala	22/1	Grey	15	71.4	13.6	33	62	93	31	33	1.5
		Merc.	16	69.3	10.3	41	59	100	41	41	1.7
	50/1	Grey	8a†	71.8	10.8	34	60	90	30	33	1.5
			b	70.8	10.8	35	61	92	31	34	1.5
			c	—	—	—	63	102	39	38	—
		Merc.	9a	68.4	9.5	43	56	98	42	43	1.7
			b	67.1	9.4	43	56	100	44	44	1.8
	23/2	Grey	4	71.0	13.8	44	57	108	51	47	1.9
		Merc.	5	68.8	9.8	58	56	138	82	59	2.5
Pima	22/1	Grey	17	63.6	13.6	38	51	84	33	39	1.6
		Merc.	18	59.2	13.0	48	46	92	46	50	2.0
	50/1	Grey	10a†	65.2	13.1	38	55	88	33	38	1.6
			b	65.5	13.0	39	56	91	36	39	1.6
			c	—	—	—	59	94	35	37	—
		Merc.	11a	62.2	12.8	47	49	98	49	50	2.0
			b	62.8	12.6	47	50	99	49	50	2.0
	23/2	Grey	6	63.9	13.2	49	52	100	48	48	1.9
		Merc.	7	56.2	12.7	68	41	137	96	70	3.4
Coker, high grade	22/1	Grey	1	68.6	12.4	32	62	91	29	32	1.5
low grade			2	49.8	10.8	40	43	68	25	37	1.6
DPL, low grade			3	51.0	11.0	38	45	70	25	36	1.6
Delfos	50/1	Grey	12	72.0	10.5	32	63	92	29	32	1.5
Stoneville 2B			13	67.8	11.5	33	57	84	27	32	1.5
Coker, high grade			14	71.7	12.8	34	63	92	29	32	1.5

* See Table VI for origin of data.

† Samples 8 and 10 were measured at three different times. The c readings, which came from curve sheet No. 4 (see Table VI), may be due to an unintentional difference in positioning the sample.

ing in terms of per cent luster. The problem of standards took considerable time, and in October 1955, the new instrument, now supplied with carefully prepared standards, was again put through its paces. After discovering the difficulty with tube replacements, adjustments were made, and in December the instrument was sent to our Clemson laboratories where it has since been used in regular testing of samples in studies of finishing tests that are being added to the regular tests made by the USDA on their standardized variety series of cottons.

Table VIII includes data on five samples of a control cotton, Coker 100W, that is processed with each group of samples. Measurements of luster are regularly made by two observers, each preparing a separate sample. As each measurement is made, the sample is rotated through 180° for a check by the observer on sample preparation. One measurement is recorded for each observer, and an average of these two measurements is used for the final value. As may be seen from Table VIII, variations in luster measurements are within about 1%, the difference between samples and operators being about on the same level.

Table IX provides further information regarding variability in measurements of luster. The samples are grouped by single varieties, by mixed varieties of Upland cottons, and are subgrouped into early, middle, and late picked samples. The number of samples in each of these groups varies from 18 to 73. For each group the average, and the standard deviation of that average, is given both for luster of raw stock fibers and for 22/1 grey yarns. The standard deviation which accompanies each average indicates the total variability for each measurement, including any variation in the samples themselves, in their preparation, and in their measurement. A standard deviation is reported also for the differences between results obtained by two operators who prepared and measured separately each sample in each group. For luster measurements on fibers the differences between samples prepared and measured by two operators seem less than differences between samples, but for the yarns the differences seem about the same for samples and for operators. For fibers the averages of luster of single varieties may possibly be less than for mixed varieties, but for the grey yarns this does not seem to hold. There seems no significant difference between averages of cottons picked in early, middle, and late season.

Since differences of 1% do not seem to be significant, as is apparent from the data in Tables VIII and IX, per cent luster will be reported for the Standardized Variety Tests in whole numbers only. The significance referred to here concerns the statistical significance of luster measurements as they are made on the Cotton Lustermeter.

At this point it may be well to indicate that this does not necessarily reflect the significant size of observations made visually. If it were possible to observe smaller luster differences than the instrument measures, then something would have to be done to increase its sensitivity, and the precision with which samples can be prepared. But this 1% level seems well within the size difference that can be observed visually. Experimental work has not yet been done to establish the relation between visual and instrumental results for low-contrast gloss measurements, but during the course of this study the feeling developed that in the 30–40% range, it would take a difference of at least 2% to be clearly evident to the observer.[5] For example, for Upland cottons

[5] R. S. Hunter, asked for his estimate of the size of luster difference that can be detected visually, replied that he believes it difficult to detect difference of less than 2% on this scale.

TABLE VIII. Individual Measurements of Per Cent Luster by Two Observers (*O*) on Five Control Samples Included in Each Group of Differently Processed Grey Yarns (Coker 100W)

	22/1 Carded yarn, % L			22/1 Combed yarn, % L			50/1 Combed yarn, % L		
No.	O_1	O_2	Avg.	O_1	O_2	Avg.	O_1	O_2	Avg.
1	31.8	30.7	31.2	32.2	31.2	31.7	33.5	33.9	33.7
2	31.0	31.2	31.1	32.0	32.0	32.0	33.0	33.0	33.0
3	32.0	31.6	31.8	33.1	33.0	33.0	33.4	32.1	32.8
4	31.6	31.4	31.5	32.4	32.2	32.3	33.3	32.2	32.8
5	31.3	30.8	31.0	32.8	31.8	32.3	32.8	32.4	32.6
Avg.	31.5	31.1	31.3	32.5	32.0	32.3	33.2	32.7	33.0

of the same yarn number it is doubtful whether one could predict which yarns would measure 30 and which 32. On the other hand, the difference between luster of Upland and of Pima yarns, which measured about 7%, was easily recognized. Thus while the instrument provides a scale that reads to tenths of a per cent, it seems sound practice to report per cent luster rounded off to the nearest whole number.

This is done in Table X, which includes averages of luster measurements for several varieties of cottons picked in the early, middle, and late season that are included in reports of the U.S.D.A. 1955 Standardized Variety Tests.[6] Data are given for raw stock, and for whatever yarns were made from each variety in the test. The number of samples tested of each variety is reported. The second group of samples contains many of the varieties in the first group that ordinarily would be carded but, for these tests, were included in the combed group.

[6] Copies of these reports may be obtained on request from the Cotton Division, A.M.S., U.S. Department of Agriculture, Washington 25, D.C. (Bulletins Nos. 152 and 167.)

For comparison with these results, we looked up Dr. Fourt's luster data for samples in the Standardized Variety cottons of the 1952 crop. The average per cent luster obtained from his measurements on 21 samples of Acala 4–40 50's grey yarns was 31.6 ± 1.1, and for mercerized yarns, 48.1 ± 1.9. For 19 Pima 50's combed grey yarns, the average was 39.1 ± 0.6, and for mercerized yarns, 56.1 ± 1.6. When compared with the data in Table X, this seems like a very reasonable check, since the cottons were from a different crop year, and the mercerization undoubtedly on a different level.

Summary

Luster may be defined as the appearance of a surface which results from its power to exhibit mirrorlike reflections. Goniophotometric curves provide information regarding the amount of light that a sample reflects at various angles when it is illuminated at a given angle. A family of goniophotometric curves exists for each sample, a different curve for each different angle of illumination.

TABLE IX. Variability in Measurements of Per Cent Luster Grouped by Single and Mixed Varieties of Upland Cottons, and by Early, Middle, and Late Pickings, for Raw Stock Fibers and for 22/1 Grey Yarns

		22/1 Grey yarns		Raw stock fibers	
Identification	No.	Avg. % luster with *S.D.*	*S.D.** of diff. between 2 operators	Avg. % luster with *S.D.*	*S.D.** of diff. between 2 operators
Coker 100W	18				
Early		31.6 ± 0.6	±0.8	58.0 ± 1.4	±0.6
Midseason		31.5 ± 0.9	±0.8	58.3 ± 0.8	±0.5
Late		31.3 ± 0.6	±0.8	57.8 ± 1.1	±0.4
DPL	38				
Early		31.1 ± 0.8	±0.9	59.3 ± 0.9	—
Midseason		31.1 ± 0.9	±0.7	58.5 ± 0.9	—
Late		30.5 ± 0.9	±0.6	59.2 ± 1.1	—
Upland cottons	43				
Early		31.3 ± 0.5	±0.8	58.7 ± 1.6	±0.4
Midseason		31.5 ± 0.8	±0.9	58.8 ± 1.5	±0.9
Late		31.3 ± 0.8	±0.9	58.8 ± 1.3	±0.9
Upland cottons	73				
Early		30.9 ± 0.7	±0.8	58.9 ± 1.3	—
Midseason		30.7 ± 1.0	±0.8	58.3 ± 1.4	—
Late		30.5 ± 0.8	±0.8	59.1 ± 1.3	—

* Each measurement reported for luster is the average of two samples, each prepared and read by a different operator. Each operator reads his sample, then turns the sample through 180° for a check. Only one reading is reported for each operator. For this table the difference between measurements by two operators was obtained for each sample, and the standard deviation of these differences was calculated as a measure of operator variation in each group of samples.

For a truly matt surface, one with zero gloss, the reflectance of light from the surface will be the same at all angles of viewing. For a highly polished surface, the reflectance will be very much higher at the exact mirror angle than at all other angles. The reflectance at this narrow band is known as the specular reflectance, while the lower reflectance at other angles is known as the diffuse reflectance. One measure of gloss, known as contrast gloss, is provided by contrasting the specular and diffuse reflectance by the ratio S/D.

For cards of parallel threads of cotton yarn, there is no single direction in which the specular reflectance is very high in comparison with the diffuse reflectance. The reflectance changes shown in the goniophotometric curves for cotton are gradual and very smooth, and thus result in low contrasts between reflectances at different angles. Taking into consideration previous luster measurements on cotton, and the indications of a number of new goniophotometric measurements, the conditions for measuring luster in the Cotton Lustermeter were established for 45° illumination, and 0° and 45° viewing, the 0° viewing to represent diffuse reflectance (D), and 45° viewing to represent specular reflectance (S). A single-number measurement, in terms of per cent luster (0 representing zero luster, and 100 representing very high luster), is provided by the formula $100[1-(D/S)]$.

A stand is provided to hold yarn samples so that they can be loaded easily into a special sample clamp. A similar sample clamp, with narrower tongue, is provided for the preparation of raw fibers for luster measurement. In order to provide for measurement of short staple cottons, the area measured is restricted to a $\frac{1}{2}$-in. square.

The new Cotton Lustermeter, an early model of an all-purpose gloss instrument that is near completion at the Hunter Associates Laboratory, satisfactorily meets the specifications laid down for it; it provides for a new and rapid method of sample preparation, and allows measurements to be made on yarns and fibers directly, easily, and rapidly. Results check satisfactorily with luster calculated from goniophotometric measurements.

Hunterlab Cotton Lustermeter, Model D16C, has been in satisfactory use at the Clemson Cotton Laboratory of the U.S. Department of Agriculture since December 1955. It has been used to measure all of the cottons of the 1955 Standardized Variety Series in this first year in which finishing tests have been added to the many other tests regularly made and published on each annual series. Based on these luster measurements, and on the goniophotometric studies reported here, the following general conclusions may be drawn regarding luster measurements on cotton fibers and yarns:

TABLE X. Luster Measurements for Several Varieties of Early (E), Middle (M), and Late (L) Picked Cottons Included in U.S.D.A. 1955 Standardized Variety Tests

Cotton variety	No. incl.	Per cent luster															
		Raw stock			Grey yarns									Merc. yarns			
					22/1 carded			22/1 combed			50/1 combed			50/1			
		E	M	L	E	M	L	E	M	L	E	M	L	E	M	L
Acala 4–42	7	60	59	60	30	31	30										
A-44	5	59	60	61	31	30	31										
Coker 100W	18	58	58	58	31	31	31										
Deltapine 15	38	59	59	59	31	31	31										
Delfos 9169	1	58	58	60	31	29	29										
Lanhart	9	57	57	57	31	30	31										
Stoneville 2B	2	61	59	60	31	30	30										
Acala 1517C	9	61	61	61	32	31	31	32	32	32	34	33	33	43	43	43
Acala 4–42	1	60	61	58	32	31	30	31	32	31	33	33	33	44	42	42
A-44	1	60	60	61	31	32	32	32	32	32	34	34	33	37	41	42
Coker 100W	2	58	59	58	32	32	32	32	33	33	34	34	34	42	42	41
Deltapine 15	2	56	58	59	31	31	32	32	32	33	34	34	34	44	41	41
Delfos 9169	5	57	58	59	31	31	32	31	32	32	33	33	34	41	41	42
Stoneville 2B	1	58	58	59	31	33	32	31	32	32	32	33	33	41	41	41
Pima S-1	4	66	66	68							40	41	40	48	51	51

1. Measurements of luster differences less than 1% cannot be detected with certainty on replicate samples nor on samples prepared by different operators. This, however, is less than the difference estimated as necessary for the visual detection of luster differences.

2. The luster level of fibers from raw stock is about 57 to 61% for the Upland varieties tested, and about 66% for American-Egyptian varieties, as represented by Pima S-1. The luster levels of grey yarns are considerably lower: about 31% for 22/1 yarns, about 33% for 50/1 combed yarns of Upland varieties, and about 40% for Pima S-1.

3. The luster of fibers does not seem to bear any close relation to the luster of yarns, e.g., the average luster of 18 fiber samples of Coker 100W measured 58%, low for luster of raw fibers; yet yarns made from these cottons average 32%, as high a luster as for any variety in the 22/1 group of grey yarns.

4. Luster of grey yarns varies, but only very slightly, with size and preparation of yarns: For one group of cottons the luster of 22/1's carded grey yarn is increased about 1% by combing, perhaps another 1% for a finer yarn, 50/1's. However, luster may be increased considerably by use of plied yarns. This is illustrated in Table VII by the Acala grey 22/1 which measured 33%, compared with 44% for the 23/2 yarn. The luster of this Acala is increased more by plying the yarn than by mercerizing: e.g., the luster of Acala mercerized 22/1 yarn is up 8% from the grey yarn, while the 23/2 grey yarn is up 11%.

5. There seems little difference in luster between cottons picked early, midseason, or late.

Since luster measurements will be made and published hereafter for cottons in the annual U.S.D.A. Standardized Variety Cotton Tests, gradually a sufficient amount of luster data will become available to provide for comparisons between varieties and crops that are not yet possible. Meanwhile, the instrument described should serve well to provide the required information.

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INDUSTRIAL SECTION

Strength Tests of Fiber Arrays[1]

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Abstract

Basic differences between tensile tests of single fibers versus similar fibers in arrays such as yarn, skeins, tow, and staple combings keep the strength of arrays from exceeding that of single fibers. The reverse holds true for strain. Moreover, experimental difficulties of achieving simultaneous straining among the fibers in an array further reduce the apparent strength and increase apparent strain, by amounts that depend on the extent of departure from simultaneity, i.e. the strain distribution in the array.

Close equivalence of group tests of strength and maximum strain to single fiber measurements can be obtained even for the wide range of slackness observed in some tow, by recourse to a parameter that is not affected by departure from simultaneity of straining, namely, the energy absorbed in rupture. Strength, maximum strain, and associated measures of variability can be calculated from energy via the tenacity-strain function for the fiber type. Good agreement with single fiber measurements has been obtained for acrylic fibers in the form of tow.

Introduction

In research, the elucidation of relationships between fiber polymer structure, mechanical parameters, and behavior in use requires a sophisticated approach, involving studies of the interactions of such variables as stress, strain, time, temperature, and outside agencies. In contrast, control of quality of fibers in production requires quick detection of deviations from the norm, but with a minimum of simple tests of high reliability.

Two properties of textile fibers widely measured, to control quality of product and for acceptance testing, are those of maximum tenacity (strength) and maximum strain (per cent elongation). These properties may be high for some fibers and fairly low for others without necessarily limiting satisfactory utilization of each in some kind of finished fabric. Wide variability in any one kind of fiber is to be avoided, however, because of the corollary implication that other properties, not necessarily evident at the moment, may also be varying, and that variation in these may adversely affect fabrication, finishing, or use. Maximum tenacity and strain have hence become established as two of a group of indices used to show relative magnitudes of deviation from an established norm over short- or long-term trends. In so doing, the pattern of the deviation may assist in locating its source.

Although the original reasons for the choice of these tests were probably in part those of ease, simplicity, and speed, for the cases of yarn, roving, and skeins, the situation is less attractive when the fibers are in the form of tow or staple. If one attempts to establish a control using a conventional strength test on tow, it is soon found that the error in replication masks all but the grossest variations arising from differences in the product. The maximum tenacity is always noticeably lower, and maximum strain higher, than the figures derived from tests of a number of single fibers of the same material (Figure 1). This comes about for the most part because the fibers of the tow are not uniformly taut at the start of a test, but range through varying degrees of slackness introduced after spinning and stretching. Hence the strain is not the same for all fibers at any time during

[1] Presented at Symposium on Stress-Strain Properties, Massachusetts Institute of Technology, Cambridge, Mass., October 4, 1954.

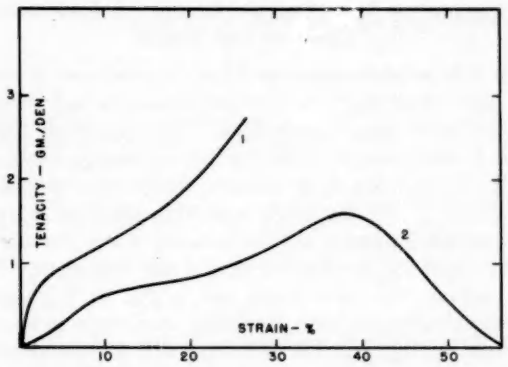

Fig. 1. Typical tenacity-strain curves for (1) single filament (2) 52000-filament tow of acrylic fiber.

a test, and a related distortion of the stress distribution occurs up to and through the region of strain where failure is taking place, leading to low apparent strength and high apparent elongation. "Simultaneous straining" of any array would, if achievable, show a maximum tenacity and associated strain representing more significantly the average performance of the entire collection of fibers, as would also single fiber tests.

Single- versus Multi-Fiber Tests

Even under ideal experimental conditions simultaneous testing of an array will not yield data equivalent to single fibers unless the stress-strain behavior is highly uniform [5]; though the fibers remain unchanged, information about their mechanical behavior can be influenced both by the test and the philosophy of calculation. One must hence decide whether the problem demands single fiber tests for their added information, but at added expense, or whether tests of arrays can be tolerated. It is well known, for example, that tests of bundles of fibers (e.g., A.S.T.M. "flat bundle" test) are subject to considerable operator influence in the preparation of the bundle [3]. The dual problems of replicate variability and slackness in an array of fibers make some device for circumventing their effects much to be desired.

Discussion-Use of an Energy Parameter

If means could be found whereby the simplicity of a direct test on arrays could be retained, but avoiding the errors noted above, an additional advantage would be gained, that of being able to sample economically the larger numbers of filament represented, rather than a score or less.

Mechanical rearrangement of fibers, as in a length of tow, to straighten slack fibers is impractical, not only because of the time required to bring about a satisfactory condition for testing, but also because of the chance of excessive breakage and stretching of the fibers. The alternative is to avoid the need to strive for simultaneous failure of the bundle of filaments by measuring a scalar rather than a vector property, i.e. a non-time-dependent quantity that can be summed sequentially, rather than one that is time dependent and hence requires that summation occur through simultaneous occurrence. This property should also bear a relation to tenacity and strain.

The energy, $E_{max.}$, to deform one or an array of fibers until rupture is complete, is such a property. The measurement of the energy E_i, expended in producing an elongation D_i, can be obtained by means of the force-distant product

$$E_i = \int_0^{D_i} F dD = \int_0^{D_i} \phi(D) dD \qquad (1)$$

where $\phi(D)$ describes the force at any elongation D of the specimen. $E_{max.}$ is obtained by substituting $D_{max.}$ for D_i. (Where the deformation takes place at a constant rate, an equivalent force-time product can be set up by taking rate of elongation, $dD/dt = k$ out from under the integral sign and making a corresponding change in the limits of integration.)

It is obvious that the same total energy will be measured whether a number of fibers is separately broken one after the other or whether they are broken together, nonsimultaneously or simultaneously.[2] In going from the first to the last case, $F_{max.}$ will increase and $D_{max.}$ will decrease. This can be extended to the case of many filaments in a tow, where the total force at any stage will be the sum of the forces being carried by each fiber at its own stage of the test, and the total elongation will be that from the time of initial tautness of the first fiber, to the point of rupture of the last (Figure 2).

If, in Equation 1, E_i is divided by W, the weight of the material under test, the following substitutions can be made:

$$\frac{E_i}{W} = \frac{1}{W}\int_0^{D_i} F dD = \int_0^{D_i/L} \frac{F}{\rho A} \cdot \frac{dD}{L} = \int_0^{\epsilon_i} \tau d\epsilon \qquad (2)$$

[2] Assuming that fibers broken together have no effect on each other.

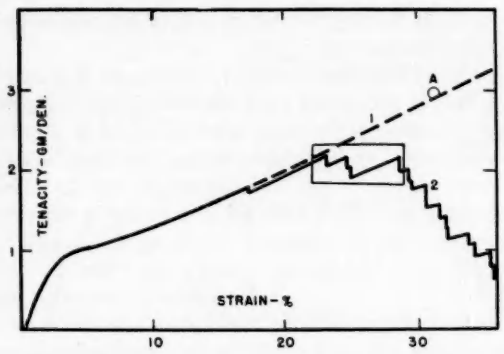

Fig. 2. Relation of (1) single filament tenacity-strain curve to (2) curve synthesized from 20 replicates, representing simultaneous straining. Compare "A" and boxed area for computed strength by single filament versus group testing.

where L is the length, A is the area of the cross section, and ρ is the density. The term ρA is the linear density, so-called. It can be seen as a result that $F/\rho A$ (or τ), the tenacity, and dD/L (or ϵ), the strain, can be employed directly to obtain the "specific energy" $E_i/W = E_{sp.}$, thus eliminating the variations in data arising from differences in weight among specimens. Suitable numerical constants provide for choices of unit.

Specific energy figures to characterize fibers are directly utilizable without the need to impose limitations on their generality. As such they can be used to describe the ability to absorb energy in various processes and uses. Furthermore, for quality control of fibers under fixed conditions of manufacture, $E_{sp.}$* can be determined more rapidly, more precisely, and with less demands on the skill of the operator, than can either flat bundle or single filament tests.

Determination of the energy expended in breaking a length of filament, yarn, or tow is experimentally simple. The specimen is stretched in a strength-testing instrument, and the energy is found either by direct recording of an index proportional to energy on an automatic integrating device, or by converting by a suitable constant from the area included under the force-elongation diagram. As a control test this method has greatest merit when an automatic integrator is used. Table I compares single fiber with tow testing for acrylic fibers, illustrating differences in all properties except specific energy to rupture.

* Asterisk indicates specific energy to rupture.

Conversion from Specific Energy to Equivalent Tenacity and Strain

It is possible under favorable circumstances to calculate from $E_{sp.}$* the maximum tenacity and strain undergone by a single fiber. To accomplish this, it is necessary to know the function $\phi(D)$, since it is this and the linear density that interrelate $E_{sp.}$, τ, and ϵ. In the single case this situation is redundant, inasmuch as it is necessary to test the fiber to determine the interrelation in the first place. If however, the fiber under test is one of a group, enough of which have previously been tested to learn their average reaction to loading and the confidence limits that can be assigned, the $[\phi(D)/\rho A]$ thus determined can be used to calculate with equivalent assurance from $E_{sp.}$* for the fiber in question, the related maximum tenacity and strain, without directly measuring the latter two parameters. This can be seen to be purely a mathematical manipulation, giving no more information than $E_{sp.}$*, merely converting it to the more familiar form of maximum tenacity and strain.

While the indirect approach just described has no practical advantage over direct measurement of maximum tenacity and strain when testing fibers singly, its usefulness is great when the principle is transferred to tests of arrays of fibers, such as tow. If $[\phi(D)/\rho A]_{avg.}$ determined from earlier tests of single fibers can be relied upon to remain constant within limits also predetermined (the case of quality control tests of a standardized product), $E_{sp.}$* found for subsequent samplings of tow can be converted to maximum tenacity and strain as described for the single fiber above. The advantage in this case lies in the fact that, through the device of direct measurement of energy, and calculation therefrom via $[\phi(D)/\rho A]_{avg.}$, the tenacities and strains determined are those that would have been found if all the fibers in the array had been strained simultane-

TABLE I. Comparison of Physical Properties Measured on Single Fibers versus Tow Acrylic Fiber

	Single fiber*	Tow
Linear density, den.	3.2	167,600
Max. tenacity, g./den.	2.6	1.4
Max. strain, %	27.0	57.3
Strain at max. force, %	27.0	41.2
Specific energy to rupture, joules/g.	34.7	32.0

* Average of 25.

TABLE II. Statistics of Single Fiber Tenacity-Strain Behavior, Acrylic Fiber, Twenty Replicates

	Strain, %										
	1	2	3	4	5	10	15	20	25	30	35
Avg. tenacity, g./den.	0.26	0.64	0.84	0.95	1.01	1.27	1.60	2.02	2.41	2.80	3.13
Std. dev., g./den.	0.11	0.15	0.17	0.18	0.18	0.23	0.30	0.39	0.43	0.54	0.62
Confidence interval, 95%, g./den.	±0.23	±0.31	±0.35	±0.37	±0.38	±0.47	±0.63	±0.81	±0.92	±1.18	±1.96
Lower confidence limit, 95%, g./den.	0.03	0.33	0.49	0.58	0.63	0.80	0.97	1.21	1.49	1.62	
Upper confidence limit, 95%, g./den.	0.49	0.95	1.19	1.32	1.39	1.74	2.23	2.83	3.33	3.98	

ously. The effect of an unknown slackness spectrum is thereby eliminated.

The function $[\phi(D)/\rho A]$ describes the tenacity-strain curve for a single fiber, $[\phi(D)/\rho A]_{avg.}$ being a corresponding curve for the average of a series of the fibers. Table II shows the data for acrylic fibers from which the average curve can be drawn; from the confidence limits shown it is possible also to plot curves representing these upper and lower limits. This has been done in Figure 3.

The relation of specific energy at any strain to tenacity and strain is best obtained graphically by determination of energy in terms of areas under any of the curves of Figure 3, at a number of selected levels of strain (or tenacity). Plotting $E_{sp.}$ versus the corresponding tenacity for the average, upper, or lower curves of Figure 3 gives the relationships illustrated in Figure 4. These then are the "master" or calibration curves for the type of fiber involved. In subsequent tests of tow produced by the same manufacturing process, the integrator provides the measure of E that can be converted to $E_{sp.}$ and used in Figure 4 to find the average tenacity and confidence limits equivalent to single fiber tests. Corresponding strain and its confidence limits are found in Figure 3.

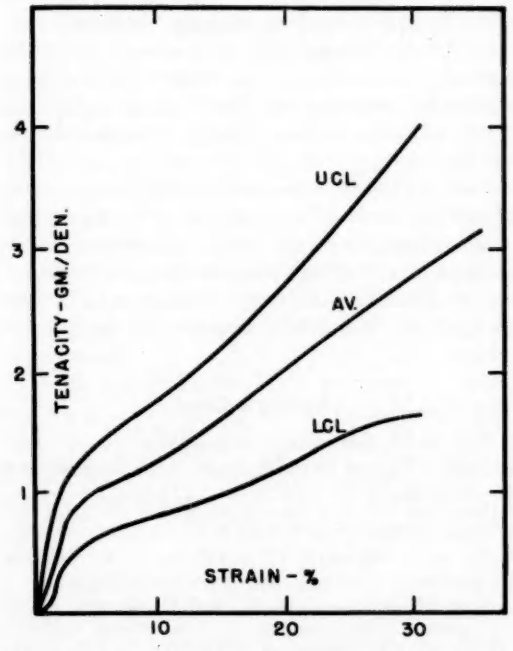

Fig. 3. Average tenacity-strain curve $[\phi(D)/\rho A]_{avg.}$ and upper (UCL) and lower (LCL) 95% confidence limits.

Experimental

Calibration of a Typical Lot of Tow

To obtain the curves shown in Figure 3, single filaments were selected from a lot of acrylic tow and tested until a satisfactory representation was obtained. This required 20 fibers.

The denier of each filament was measured on the Vibroscope [2], followed by tenacity-strain curves

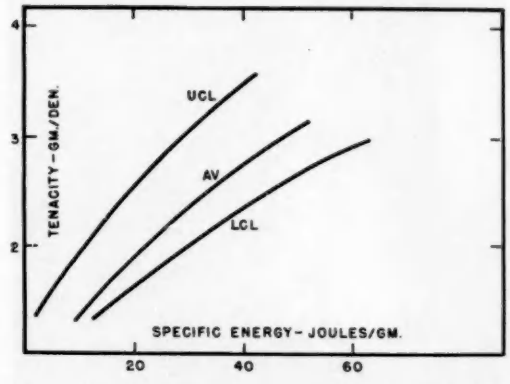

Fig. 4. Specific energy versus tenacity for acrylic fiber. Derived from Figure 3.

using the Instron [1] apparatus, calibrating to a full-scale reading of 5 g./den. for each fiber. A strain rate of 45%/min. was used; constant conditions were maintained at 23° C. and 50% R.H. The condensed data from these curves are shown in Table II.

Figure 4 was obtained from Figure 3 by measuring areas in 5% increments of strain from 10 to 35%, making the necessary calculations to obtain the specific energies at these points and plotting versus tenacity.

The master curves are valid only for material produced under constant conditions. If a change is made in the method of fiber production, the shapes of the strain-tenacity curves of the resulting fibers should be compared against those of fibers for which master curves have been established. This can be done by obtaining tenacity-strain curves for 10 to 20 filaments from the new fiber lot, then matching them visually to the curves of the established lot. If a reasonable match cannot be obtained, new master curves must be set up for the new production.

Tests of Production Tow versus Single Fibers

Conditions for tests of tow were the same as for single filaments. Each test used a length of 1 m., which was weighed to establish the denier. The Instron apparatus was calibrated to read in tenacity, and strain and specific energy were based on a test length of 10 in. The tow was gripped by wrapping on nonrotating tapered capstans, as shown in Figure 5, tying to posts beyond each capstan. This minimized slipping as well as virtually eliminating "jaw breaks"; the tapered capstans prevented wrapping over and self-damage. A small constant error, caused by assuming that only the material from center to center of the capstans participated, was ignored.

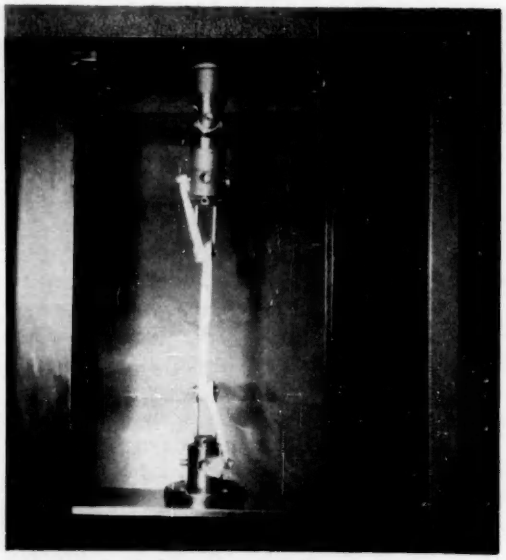

Fig. 5. Capstan grips for energy tests of tow.

TABLE III. Comparison of Direct Measurement versus Calculation from Tow Test, of Tenacity and Elongation

	Single filament tensile test*		Tow test*		
Doff No.	Avg. max. tenacity, g./den.	Avg. max. elong., %	Energy, joules/g.	Avg. max. tenacity, g./den.	Avg. max. elong., %
1	3.0	31.0	56.1	3.2	35.5
2	3.0	34.0	51.8	3.1	34.5
3	3.0	31.0	51.7	3.1	34.5
4	2.9	31.5	55.8	3.2	35.5
5	3.0	35.0	52.6	3.2	34.5
6	3.1	33.0	53.1	3.2	35.0
7	3.3	29.5	54.1	3.2	35.5
8	3.3	36.0	51.3	3.1	34.0
9	3.3	33.0	51.3	3.1	34.0
10	2.7	32.0	48.8	3.0	33.0
11	2.7	32.5	49.6	3.1	33.5
Avg.	3.03	32.6		3.14	34.5
Std. dev.	0.21	1.8		0.06	0.8

* Five replicates tested for each doff.

Table III records the average strain and tenacity figures for eleven doffs as determined by the average of five single filaments, versus the average values obtained by calculating from the energy expended to rupture five lengths of tow. Ranking tests indicate no significant differences between the two sets of values.

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Manuscript received August 28, 1956.

National Cotton Council of America

The Fifth Chemical Finishing Conference

The following four papers were presented October 4, 1956, in Washington, D.C. Papers presented October 3, 1956, will appear in the March issue of TEXTILE RESEARCH JOURNAL.

A Simplified Relationship between the Properties of Resin-Finished Cotton Fabric and the Solids Applied

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Introduction

A year ago it was our privilege to present to the Finishing Conference of the National Cotton Council a paper "Variables of Cure in the Resin Finishing of Cotton" [1]. With the increasing importance of crush-resistant finishes brought about by the industry's promotion of wash and wear cottons, the work reported at that time was continued in order to get a better understanding of how different resins behave, as well as to improve the procedure for evaluating the effects of thermosetting finishes on cotton. As a result some new relationships have been uncovered between fabric properties and resin solids applied.

It has been found that fabric properties of wrinkle recovery, tensile strength, and tear strength vary directly as the logarithm of the resin solids applied. In addition, at a constant resin solids applied the same properties also vary as the logarithm of the catalyst concentration, but over a much narrower range.

In the earlier work, the effects of cure temperature, catalyst concentration, and cure time were investigated at a number of solids levels for a cyclic ethylene urea resin and a methylated methylol melamine resin. The points for wrinkle recovery fell along a curve such as is shown in Figure 1.

This method of evaluation was adopted at that time in order to obtain a more accurate comparison of the effectiveness of different resins in producing wrinkle recovery. It also provided a reasonably reliable means of studying the effect of such variables as catalyst concentration, cure temperature, and cure times.

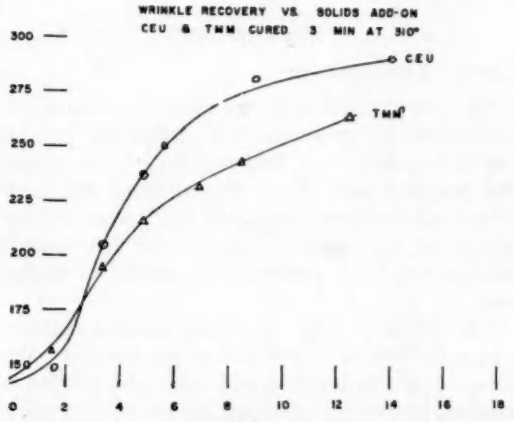

Fig. 1.

Although the method tended to reduce the effect of fabric variability, and the differences between operators in resin application and measurement of fabric properties, the fact that the results fell along a curve was considered less desirable than a relationship which would result in a straight line plot. After the data were replotted in other ways, it was apparent that if wrinkle recovery was plotted against the logarithm of resin solids-on, much of the data fell along a straight line. Deviations were noted at low solids-on and at high solids-on. This was believed due to the fact that catalyst concentration was taken as a percentage of resin solids. This meant that the amount of catalyst in the bath and on the fabric varied as resin solids varied.

Application and Testing Procedure

In all of the work carried out in this study, an 84 × 76 pure finish cotton was used. The fabric samples, measuring approximately 23 in. on the warp by 17 in. on the filling, were impregnated with resin solution while flat, padded at 160 lb. per linear inch, framed under mild tension, dried 3 min. at 200° F., followed by the curing step, conditions of which were varied. The cured samples were given a refinish wash, and drip dried, i.e., hung on a line directly from the wash without centrifuging. Wrinkles were removed by pressing on a flat bed press.

After conditioning for 24 hr., samples were tested. Wrinkle recovery was run on the Monsanto Wrinkle Recovery Tester, tensile strength (lb.) on the J-2 Scott Tester, and tear strength (g.) on the Elmendorf Tear Tester.

Experimental

Catalyst Concentration

In order to determine the effect of catalyst concentration, an experiment was carried out in which the resin solids were held constant, while varying the catalyst concentration. It was found that a plot of wrinkle recovery (warp and fill) versus the logarithm of the catalyst concentration fell along a straight line for a portion of the spread of catalyst concentration.

This attack was then expanded, using a reactant-type resin with an organic amine–type catalyst. One would expect that with a very low concentration of catalyst, regardless of resin solids concentration, there would be no improvement in wrinkle recovery due to the fact that fabric and resin alkalinity would neutralize the catalyst. One would also expect that at some higher catalyst concentration, the maximum wrinkle recovery would be obtained and that further additions of catalyst would not increase it further. As shown in Figure 2, this proved to be the case. In this experiment 9% resin solids in the bath were applied to give 7.9% solids on fabric. The catalyst concentration was varied from 0.03 to 4.0% in the bath, giving a catalyst concentration on the fabric of from 0.027 to 3.6%.

This has been plotted as two straight lines, rather than a curve. The transition from a straight line sloping upward to a horizontal line is rather abrupt, and for convenience we have somewhat arbitrarily chosen to draw it in this manner. Studies of this type over the range of resin solids 2 to 20% and cure temperatures of 270° to 330° F. showed that with the fabric we were using, maximum wrinkle recovery was obtained with 0.4 to 1.0% catalyst product on the bath, or roughly 0.1 to 0.3% amine hydrochloride solids on the bath. Obviously if the fabric has more residual alkali present, more catalyst will be required.

Figure 2 also shows the effect of cure temperature on the wrinkle recovery as the catalyst in the bath is increased. It will be noted that the maximum wrinkle recovery attained is the same for the 270° cure as the 310° cure. The only difference is that less catalyst is required at the higher cure temperature. For example, with the 310° cure the maximum wrinkle recovery is attained with 0.5% catalyst on the bath, while at 270° about 1% catalyst is required to give the peak wrinkle recovery.

In earlier work, catalyst had been taken at 10%

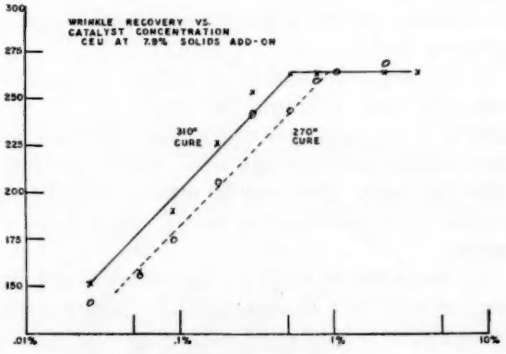

Fig. 2.

of resin solids, so that at low resin concentrations, the catalyst concentration had been below that necessary to give complete utilization of the resin. By taking catalyst concentration as a percentage of the bath, deviations at low resin solids were markedly reduced.

In Figure 3 is the plot of catalyst concentration versus tensile strength. At any given solids level, tensile strength decreases as a straight line function of the catalyst concentration up to the point where sufficient catalyst is present to cause all the resin to react.

This study served mainly to show that with the fabric we were using a complete cure would be assured with 1% catalyst product on the resin bath.

Effect of Resin Solids

As was pointed out above, a replot of earlier data indicated strongly that wrinkle recovery, tensile and tear strengths varied directly with the logarithm of the solids-on. Several series were then run in which fabric samples were treated at different resin solids levels using 1% catalyst product on the bath. Ten levels of resin solids were used between 1.2 and 20% on the bath, so that points were spaced fairly evenly on the log plot. (1.2, 2, 3, 4, 6, 8, 10, 12, 16, and 20% were preferred.)

Figure 4 is the plot of warp plus fill wrinkle recovery against the logarithm of the CEU resin solids-on at three different curing temperatures. Again, this is drawn as two straight lines (one sloping upward, the other horizontal) rather than a curve. It will be noted that the break in the line comes at a solids-on of approximately 11 to 12%,

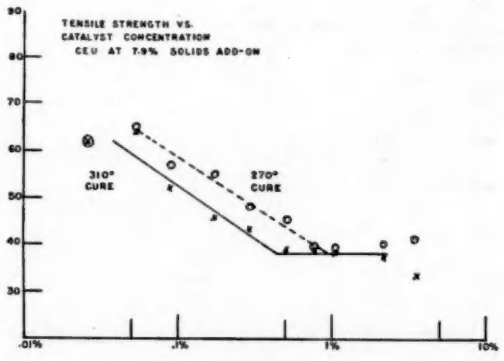

Fig. 3.

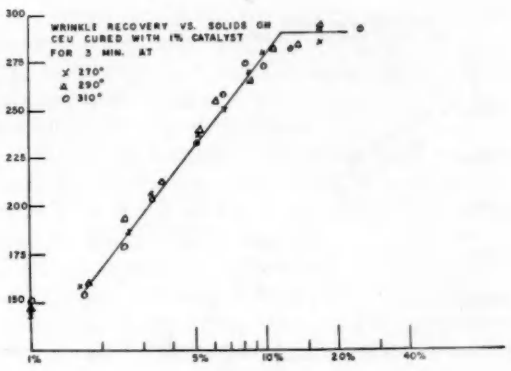

Fig. 4.

and that increasing the solids above this is almost no benefit.

These data along with similar data have been examined statistically in the range between 1.7 and 10% CEU solids-on. Over this range correlation analysis of these data indicated a straight line relationship of extremely high significance.[1]

It is also significant that above 11 or 12% resin solids-on, the wash and wear characteristic deteriorates. A phenomenon that is best described as a cracky appearance develops as the resin solids-on go above this level.

Figure 5 shows the tensile strength for the same treatments represented in Figure 4. The deviation of points from the straight line between 1 and 10% solids appears greater than in the case of wrinkle recovery. This is probably due to the fact that a

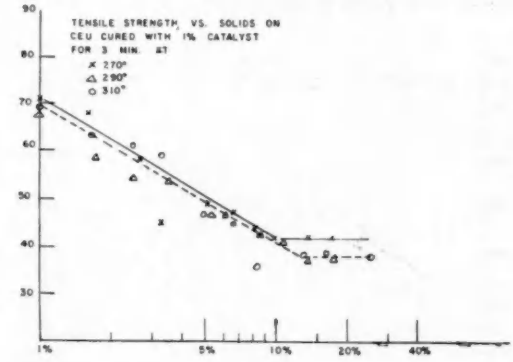

Fig. 5.

[1] The criterion for correlation used here is 99.9% confidence level.

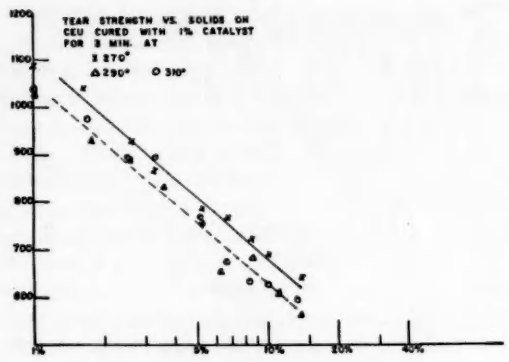

Fig. 6.

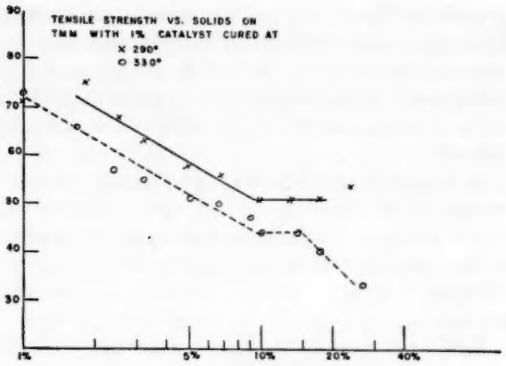

Fig. 8.

cut strip rather than ravelled strip was used in the tensile tests.

Figure 6 represents the tear strength, also for the same treatments, and again the data fall along a straight line.

A methylated trimethylol melamine was then investigated in a similar manner. The catalyst concentration to give maximum wrinkle recovery ran from about 0.3% catalyst product at 4% resin solids-on to 1% at 20% resin solids-on.

The plot of wrinkle recovery versus solids-on is shown in Figure 7. A 330° cure gives on the order of 10° better wrinkle recovery (warp and fill). You will note that above about 14 to 15% resin solids-on there is practically no increase in wrinkle recovery, while with the CEU resin this occurred around 11 or 12% solids-on. Tensile strength and tear strength are lowered by the higher curing temperature, as shown in Figures 8 and 9.

Practical Aspects of the Logarithmic Relationship

The fact that a straight line relationship exists over the practical range of resin solids applied has made the comparison of different resins much simpler.

It is considerably easier to assess the significance of differences between the slopes of two straight lines than the difference between two curves of the same general shape. In Figure 10 is a comparison of wrinkle recovery of three different resins. The best one is the CEU resin, while the other two are methylated methylol melamines of different degrees of advancement, the lower curve being the more advanced resin. Obviously, the more advanced material contains less of the component that is capable of penetrating, with the result that a smaller proportion of the resin solids is available for cross-linking.

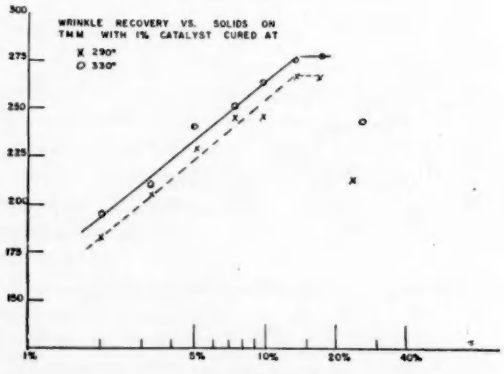

Fig. 7.

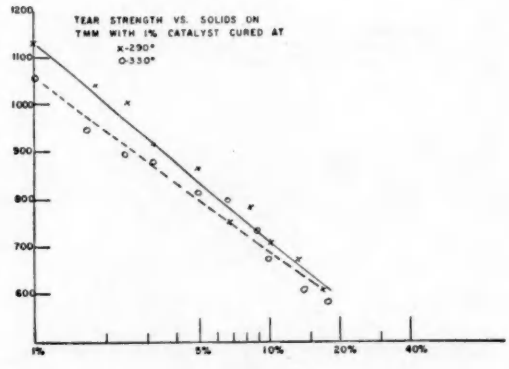

Fig. 9.

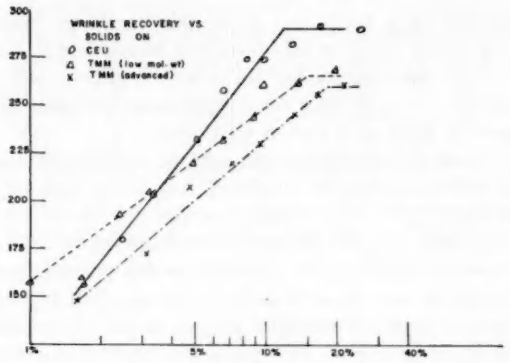

Fig. 10.

On the other hand, more of it remains on the surface to modify hand.

Correlation analysis of these data for the three plots in Figure 10 confirms the straight line relationship over the practical range. The transition from the straight line to the horizontal line is probably not as abrupt as the graph would suggest.

There is some evidence, however, that beyond this transition region, a different reaction predominates.

We have also found the method very useful in preparing fabrics with equal increments of wrinkle recovery to use as wash and wear standards. In this connection, it is interesting to note that fabrics below approximately a 4% level of CEU resin solids exhibit marked wrinkling, if washed and drip dried, while fabric treated with higher CEU resin solids are rippled, but have far fewer wrinkles. The transition from one to the other occurs at a CEU resin solids-on of about 4%.

In Figure 11 is the relationship of wrinkle recovery to the wash and wear standards we use. The basis of this and the interrelationship of wrinkle recovery with wash and wear was discussed in a recent paper by C. R. Williams [4].

The No. 1 standard was actually not washed, while all others were drip dried after a 160° F. wash. No. 9 was an untreated cotton. None of the samples was pressed in any way.

As was mentioned earlier, resin solids above 11 or 12% cause a deterioration of the fabric appearance. This is one of the bits of evidence suggesting that beyond the transition region, a reaction mechanism different from that at lower solids add-on predominates.

Still another useful application of the straight line relationship is in calculating resin costs for a given degree of wrinkle recovery. In Figure 12 is plotted the wrinkle recovery against log of solids-on for two resins—a commercial resin, Resin A, and experimental material, Resin B. For purposes of illustration, the cost per pound of solids has been taken at 60¢ for Resin A, and 40¢ per solid pound for Resin B. It is also assumed that a fabric weighing 5 oz./sq. yd. is to be treated. The cost of the resin on 100 sq. yd. of fabric is then as shown. For a warp plus fill wrinkle recovery of 200°, Resin B is less expensive than A. But at 225° recovery they are equal, while at a 250° wrinkle recovery the cost with Resin A is lower. The method provides a means of distinguishing the glitter from the gold.

If one wished to determine the effect of fabric construction on wrinkle recovery, we feel the method would be helpful. In Figure 13 is a comparison of

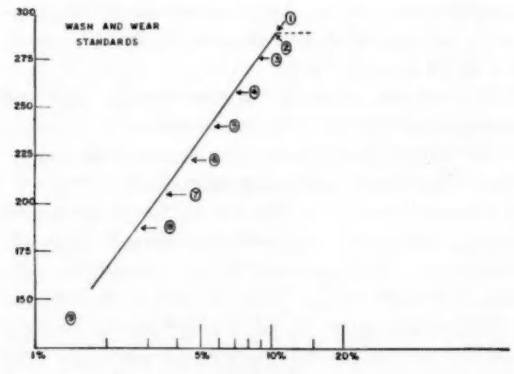

Fig. 11.

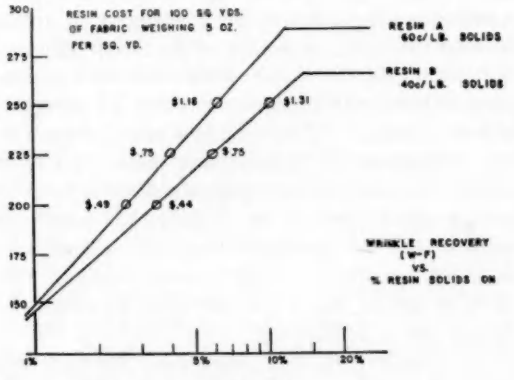

Fig. 12.

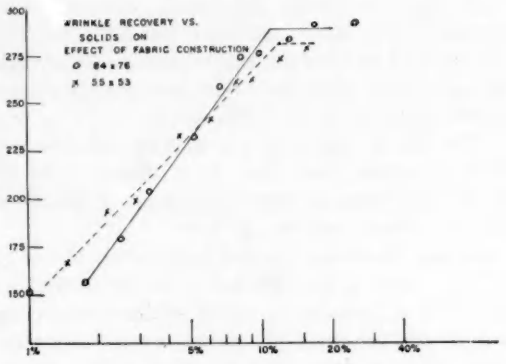

Fig. 13.

two different plain weave cottons: one is an 84 × 76 with 38's in the warp and 45's in the fill, as determined on the pure finish fabric just as we receive it. The other is a 55 × 53 sheeting with 16's in the warp and 18's in the fill. The difference is not great. It is shown merely to point out that fabric construction can influence wrinkle recovery.

We have presented a brief outline of some of the more practical uses to which we have put this concept in our laboratory. The data that have been presented are typical of many such runs.

Theoretical Speculations

It was noted that the CEU resin seemed to reach its peak at a resin solids-on of 11 to 12%. The question might then be raised "Is there any particular significance to this?"

If, for the sake of calculation, the 11% solids add-on is taken as that corresponding to peak wrinkle recovery, and if the accessibility of cotton is taken at 44%, as estimated by Mark [3] and Howsmon [2], a simple calculation reveals that there is 1 mol of CEU resin for every 3.8 accessible glucose residues. If the cellulose cross-linking theory is accepted, this figure comes surprisingly close to one cross-link for each pair of cellobiose units in the accessible areas of the cotton. Or putting it another way, one methylol group has reacted with each cellobiose unit in the accessible regions. To be more precise, this works out to be 1.12 methylol groups per cellobiose unit.

In the case of the melamine resin, TMM, it will be recalled that the wrinkle recovery peak occurred around 14% solids-on. With this particular resin (assuming all of it is monomeric which is not the case), 1 mol is combined for every 5.6 glucose units, which is not in very close agreement with the 3.8 glucose units to 1 mol of CEU resin.

If, on the other hand, the ratio of methylol groups to cellobiose units is calculated, it is found that 1.22 methylol groups are combined per cellobiose unit. The resin analysis did not differentiate between formaldehyde present as a methylene bridge and that present as a methylated methylol group. The higher ratio of apparent methylol groups to cellobiose unit could be accounted for by the presence of HCHO in other than the methylol form. In other words, a methylene bridge would appear as formaldehyde in the analysis, but such a bridge could not take part in the cross-linking reaction, or could conceivably occur only in those species incapable of penetrating the cellulose fiber to form cross-links. It might be said perhaps that the apparent ratio of methylol groups to available cellobiose units at the resin solids levels giving maximum wrinkle recovery is a measure of efficiency of the material as a cross-linking agent. The lower the number the more effective the cross-linking, with a figure of 1.0 being the ultimate.

These results suggest that in the cases of a methylated trimethylol melamine all three of the methylol groups take part in the cross-linking reaction with the cellobiose units.

Summary

It has been shown that in the resin treatment of cotton to achieve wrinkle recovery using an amine hydrochloride catalyst, the wrinkle recovery at a constant resin solids deposit increases as the logarithm of the catalyst concentration between about 0.1 and 1% on the bath.

The wrinkle recovery, tensile strength, and tear strength vary linearly as the logarithm of the resin solids deposited up to a point beyond which additional resin does more harm than good.

The relationship has been found of value in predicting the performance of resin-treated cotton, in comparing different resins on a price performance basis, in studying the effect of fabric construction and cure conditions in producing wrinkle-resistant cottons, and in the development of wash and wear cottons.

Evidence has been presented which indicates that wrinkle recovery is produced by cross-links between pairs of cellobiose units in the accessible regions of the cellulose.

Acknowledgment

The author wishes to express his appreciation to C. L. Kingsford, who carried out the application and testing work involved in this study.

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Epoxy Resins in the Crease Proofing of Cotton

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Shell Development Company, Emeryville, California

THE epoxy resins are an entirely new class of compounds for the crease proofing of cotton [1] unlike any other commercially available crease-proofing resin. The most outstanding feature of the epoxy resins is the fact that they are absolutely non-chlorine-retentive. The three features which make them different are (1) the presence of an epoxide or oxirane ring, (2) the absence of nitrogen, and (3) the absence of formaldehyde. All of the well-known resins which impart a substantial degree of crease resistance do contain formaldehyde; therefore some have felt that the material used is merely a carrier for formaldehyde which is liberated to give the noted effects. The fact that epoxy resins do give crease resistance while they contain no formaldehyde should help to dispel this theory. The absence of formaldehyde is also of practical value, in that odor development which may occur with nitrogen-formaldehyde resins cannot occur with epoxy resin-treated fabrics.

The absence of nitrogen overcomes the problem of chlorine retention. Since the epoxy resins contain no nitrogen, they are absolutely non-chlorine-retentive and it is now possible for the first time to obtain a crease-resistant white fabric which can be bleached and ironed without scorching or loss of strength. Furthermore, this non-chlorine-retentive property is not destroyed by repeated hot alkaline washing or by repeated washing and chlorination, as is the case with "chlorine-resistant" types of nitrogen-formaldahyde resins.

Replacement of the methylene-nitrogen linkage, which can be rather easily hydrolyzed, with the carbon-to-carbon linkages in the epoxy resins gives a finish which is much more durable to repeated launderings. In addition to durability, non-chlorine-retention, and freedom from odor, the treated fabric has a soft silky feel with a high gloss.

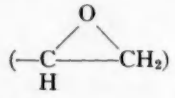
Processing

The process for the production of epoxy resin–treated goods is essentially the same as that being used for other types of fabrics. The application of epoxy resins to cotton fabric is carried out with conventional equipment using conventional drying and curing schedules. The fabric is padded through a mix of desired solids content and squeezed to give the desired solids pickup on the fabric. The fabric is then dried in a clip or tenter frame for about 2 min. at 240° F. Although we have not dried on cans, this may be entirely possible since resin migration has never been a problem. Drying at a variety of temperatures has always given soft fabrics, indicating that resin migration does not take place. The dried fabrics are then cured. Cure can be carried

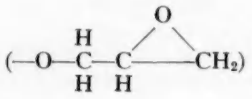
out at various elevated temperatures depending on cure time. For instance, at 320° F. full cure requires 5 min., whereas at 375° F. cure is accomplished in about 1 to 1½ min. White fabrics have a slight yellow hue after cure, but this is removable by bleaching in peracetic acid, hydrogen peroxide, or sodium perborate.

Chemical Nature of Epoxy-Containing Compounds

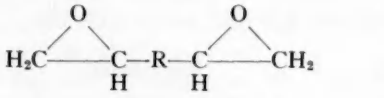
The reactive portion of an epoxy resin is the epoxy group or oxirane ring



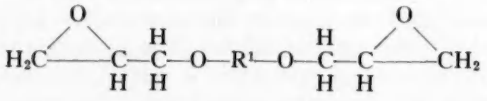
In some commercial resins the oxirane ring is attached to an oxymethylene group giving a glycidyl group



Polyfunctionality is necessary, however, to obtain cross-linking so the resin being used should contain at least two epoxy groups linked through an intermediate group R or R^1, as shown in compounds 1 and 2.



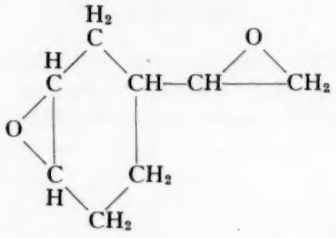
(1)



(2)

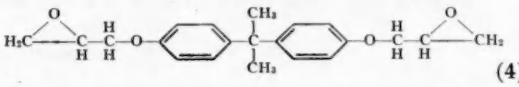
These intermediate groups R and R^1 can be almost anything to give a variety of end products useful in the treatment of textiles or in the preparation of castings, laminates, surface coatings, etc. For the crease proofing of white cotton, however, the central group should not contain nitrogen if the non-chlorine-retentive features of the resin are to be retained. In addition, nitrogen-containing compounds act as catalysts and curing agents so that short shelf life would be encountered.

For instance, R or R^1 could be a hydrocarbon or a polyhydric phenol, a polyhydric alcohol, or an inorganic acid, such as phosphoric acid. As an example, if R were a hydrocarbon, one might have vinylcyclohexene dioxide, compound 3.



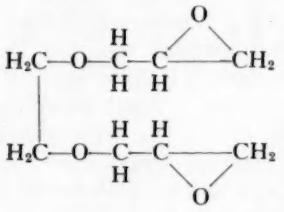
(3)

If R^1 were a phenol such as bisphenol A, one could obtain the digylycidyl ether of 2,2-bis (p-hydroxyphenyl) propane, compound 4.



(4)

Likewise, if R^1 were a polyol such as ethylene glycol or sorbitol, one could obtain the digylycidyl ethers of ethylene glycol [3] or sorbitol, compounds 5 and 6.



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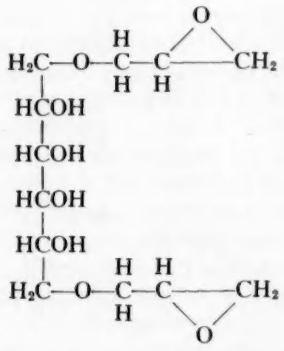
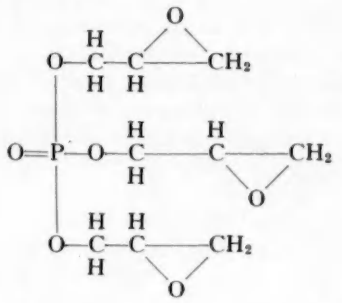


(6)

In the same fashion, if R^1 were an acid group such as phosphoric acid, the epoxy resin would be the triglycidyl ester of phosphoric acid, compound 7.



(7)

With polyols it is theoretically possible to attach as many glycidyl groups as there are hydroxyls. For instance, with sorbitol, it is theoretically possible to attach six glycidyl groups. In practice, however, fewer groups than this would be attached.

Quite a number of epoxy-containing compounds have been synthesized and evaluated in the crease proofing of cotton. As would be expected, these compounds have varying degrees of effectiveness. As an illustration, Table I shows the crease recovery [1] obtained on 80 × 80 cotton print cloth with seven widely different types of experimental compounds. As can be seen, they range from practically ineffective (No. 829) to very effective (No. 623). Based on over-all performance, cost, and other factors Experimental Resin 694 was selected as being the best candidate, and it is now being marketed under the name of Eponite [2] 100.

TABLE I. Crease Recovery Produced by Various Experimental Epoxy Resins

Experimental epoxy resin	Crease recovery avg. W and F
1675	111
694	125
682	126
685	111
639	117
829	83
623	133

Physical Properties of Epoxy Resins

Typical physical properties of epoxy resins are shown in Table II. Those above the line are common to all the epoxy resins, while those below the line can vary from resin to resin. Epoxy resins are 100% reactive materials. Since they are not solutions or emulsions, freezing has no effect on them. Because they are less reactive than methylol-containing resins, their storage stability is excellent. They are essentially neutral but may on occasion be slightly alkaline. They have a slight but not unpleasant odor. Viscosity and color vary over quite a range depending on the R or R^1 used to connect the epoxy groups. For Eponite 100, viscosity is kept within 90–150 centipoises.

TABLE II. Physical Properties of Epoxy Resins

Resin solids	100%
Effect of freezing	None
Storage stability	Excellent
pH	Neutral
Odor	Slight
Viscosity	100–15,000 centipoises
Color	1–10 Gardner
H_2O solubility	Variable

Water solubility also varies depending on R. Vinylcyclohexene dioxide for instance has a solubility of about 9%. Eponite 100 on the other hand is largely water-soluble but does contain a difficulty soluble fraction. Both the easily soluble and the difficulty soluble fractions are equally useful in this application, however. Consequently, the poorly soluble portion is not separated but is emulsified during the preparation of the pad mix. Emulsification is not an arduous task, but we realize that complete water solubility would be much preferred, so work is being carried out in an attempt to modify the synthesis to give complete water solubility.

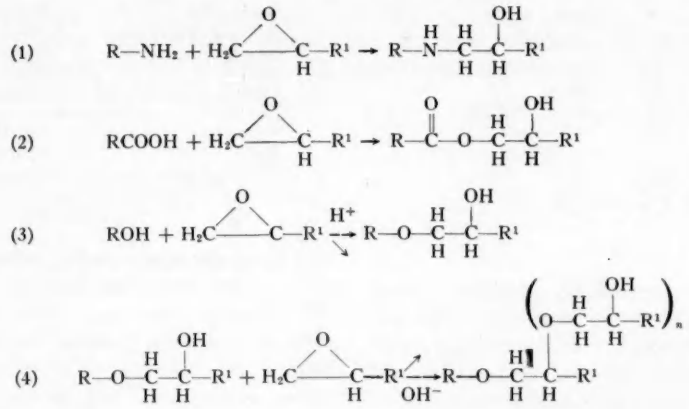
Chemical Reactivity of Epoxy Resins

Epoxy-containing compounds react with a variety of other compounds and with themselves to give polymeric products, if both the epoxide and co-reactant are polyfunctional. Some of these materials, as shown in Table III, include amines, carboxylic acids, and alcohols. As can be seen, a secondary hydroxyl is always formed as a result of the addition. In the reaction with a primary amine, a secondary amine is formed which can react with another epoxide. With diprimary amines and diepoxides highly cross-linked polymers are formed. With carboxylic acids an ester

[1] AATCC Tentative Test Method 66–56, Monsanto Wrinkle Recovery Test.

[2] Trade mark Shell Chemical Corporation.

TABLE III. Chemical Reactivity of Epoxy Resins



group is also formed. With dicarboxylic acids of moderate strength and a diepoxide, linear polymers are obtained. If one employs a strong acid such as oxalic acid, cross-linking will occur giving an insoluble cross-linked polymer. Reaction with alcohols gives a primary ether in addition to the secondary alcohol. If a polyhydroxy compound such as glycerine is used with a diepoxide, a cross-linked polymer is obtained. Cellulose, a polyhydroxy compound apparently reacts in the same way.

The reaction of amines and carboxylic acids with epoxides is very fast and no catalyst is required. Reaction with alcohol or polymerization is very slow, however, and here a catalyst is needed. Primary or secondary amines or carboxylic acids do not act as catalysts for the reaction of epoxides with alcohols or the polymerization of epoxides since they react quickly with the epoxides to form the amine adducts or esters. Thus, if you had a mixture of an epoxide, an alcohol, and an amine, you would obtain the amine adduct with very little if any ether formation. Polymer of this type deposited in or on fabric is useful in some applications, but it does not produce crease resistance in cotton.

Materials which catalyze the reaction of alcohols with epoxides, also catalyze the polymerization of epoxy groups in a varying degree depending on the material used. As can be seen, the product formed by the addition of an alcohol or water to an epoxide is the starting point for the polymerization reaction in Equation 4. The secondary alcohol formed is capable of reacting with another epoxy ring to give another ether and another secondary hydroxyl which can add still another epoxy group.

The ratio of ether adduct to polymer formation depends on a number of things. These are:

1. Type of alcohol
2. Concentration of alcohol
3. Type of catalyst

If a primary alcohol is used and the proportion of alcohol to epoxide is relatively high, the product will be predominantly ether. Conversely, if a secondary alcohol is used or if the proportion of alcohol is low, polymerization is favored.

Catalysts suitable for this reaction are strong alkalies, tertiary amines, mineral acids, or acid-liberating salts. Strong alkalies and tertiary amines give predominantly polymer formation with some ether formation. For instance, in the reaction of equimolar concentration of phenyl glycidyl ether and isopropyl alcohol catalyzed with either potassium hydroxide or benzyldimethyl amine, 80% of the isopropyl alcohol was recovered [2].

Strong acids or acid-liberating salts favor ether formation. For instance, in the same reaction the use of stannic chloride [2] or boron trifluoride etherate gave very little unreacted isopropyl alcohol. The use of strong acids for the reaction of epoxies with cellulose is out of the question, however, since severe loss in strength is encountered. This leaves the acid-liberating salts, which have proven very effective.

If one applies 10% of Eponite 100 to cotton fabric, the proportion of hydroxyl to epoxy is about

26 to 1. Considering only the primary hydroxyls in cotton, the proportion is still 8 or 9 to 1. With this high proportion of alcohol groups to epoxy groups coupled with an acid-liberating catalyst, we feel fairly confident that cellulose cross-linking is predominant in this system and that polymer formation is relatively low. In addition, the treated fabrics are insoluble in cellulose solvents such as Triton B (trimethyl benzyl ammonium hydroxide) or cuprammonium solution, and they exhibit immunization toward direct dyes.

Catalysis

Since epoxy groups are less reactive than methylol groups, catalysts which are ordinarily used with nitrogen-formaldehyde resins are not effective for epoxy-containing compounds. For instance, the amine hydrochlorides, metal halides, or ammonium phosphate do not produce the desired effect. Stronger catalysts such as the fluoborates, perchlorates, or sulfates are required.

The fluoborates and sulfates have been studied in detail. It has been found that the catalytic activity of the amine fluoborates depends on the basic strength of the amine used. That is, the weaker the amine the better the catalytic activity. For instance, the fluoborate of diethyl aniline (which has an ionization constant of 3.8×10^{-10}) is an effective catalyst, whereas the fluoborate salt of triethyl amine (which has an ionization constant of 5.6×10^{-4}) has very little catalytic activity. These amine fluoborates, however, impart color to the fabric so are of little value.

The metal fluoborates on the other hand behave in the same manner but do not impart color. A number of metal fluoborates have been examined to determine their catalytic activity (Table IV). This was carried out by impregnating 80 × 80 print cloth with 15% emulsions of epoxy resin which would give about 10.5% resin pickup. In each case the amount of metal salt used was equivalent to 5 parts of fluoboric acid per hundred parts of epoxy resin and the pH of the pad bath was kept between 3.0 and 4.0 to avoid pH effects. It was found that zinc, magnesium, and aluminum fluoborates were excellent catalysts. Copper, nickel, and cadmium were fairly active. Lead, tin, and mercury were moderate. Calcium and beryllium fluoborates showed mild catalytic activity, while potassium and sodium showed practically none.

Certain selected metal sulfates were also examined to determine their catalytic activity (Table V). Again 80 × 80 print cloth was impregnated with a 15% emulsions of epoxy resin which gave about 10.5% of resin add-on. Rather than keeping the concentration of sulfate radical constant as in the case with fluoboric acid, the concentration of sulfate radical was varied in an attempt to determine optimum catalyst concentration. The solutions were also used at the pH obtained rather than adjusting to a constant pH. As in the case of the amine fluoborates, it was found that catalytic activity was dependent upon the basic strength of the metal used. Sulfates of weakly basic metals gave high crease recovery at relatively low concentrations, whereas the sulfates of strongly basic metals gave poor crease recovery even when high concentrations of the salts were used. The relative order of the metal sulfates does not correlate with the order obtained with the fluoborates. For instance, zinc and aluminum fluo-

TABLE IV. Catalytic Activity of Various Metal Fluoborates

Metal fluoborate	Crease recovery avg. W and F
Zinc	132.5
Magnesium	130.5
Aluminum	125.0
Copper	122.5
Nickel	122.5
Cadmium	119.0
Lead	116.0
Tin	115.0
Mercury	114.0
Calcium	103.5
Beryllium	96.5
Potassium	89.5
Sodium	89.0
Untreated cloth	84.0

TABLE V. Catalytic Activity of Various Metal Sulfates

Catalyst	PHR	PHR acid radical	pH	Crease recovery	Tensile
$Ce(HSO_4)_4$	5.0	3.71	1.3	—	V. weak
$Al_2(SO_4)_3 \cdot 18H_2O$	8.1	3.50	3.4	130	25.0
$BeSO_4 \cdot 4H_2O$	4.62	3.50	3.1	129	27.9
$FeSO_4 \cdot 7H_2O$	10.0	3.46	3.5	120	43.1
$CuSO_4 \cdot 5H_2O$	9.34	3.5	4.5	113	39.1
$CuSO_4 \cdot 5H_2O$	13.0	5.0	4.5	117	38.8
$ZnSO_4$	8.4	5.0	5.7	112	47.9
$ZnSO_4$	16.8	10.0	5.7	114	43.3
$ZnSO_4$	16.8	10.0	3.5	108	42.0
$CdSO_4$	20.0	9.1	5.4	95	49.9
$NaHSO_4 \cdot H_2O$	20.0	13.9	1.0	95	49.9

borates had about the same effectiveness, whereas aluminum sulfate was more active than zinc sulfate.

The salts of very weak metals cannot be employed, however, since excessive tendering of the fabric is encountered. For instance, cerric hydrogen sulfate gives a very weak fabric. Aluminum and beryllium sulfates give good crease resistance but tensile loss is very great. Ferrous sulfate gives a good ratio of crease recovery to tensile strength but unfortunately color is produced, as would be expected. Zinc sulfate gives fair crease recovery and of the sulfates appears to offer the most promise. Sulfates of strongly basic metals such as cadmium show only mild catalytic activity.

Since the decreasing effectiveness may have been due to increasing pH, zinc sulfate was evaluated at a pH of 3.5 to compare with the pH of 5.7 obtained without pH adjustment. The crease recovery and tensile strength obtained at a pH of 3.5 was comparable to that obtained at 5.7, showing that acidity of the bath is not the factor determining catalytic activity. This is partially substantiated by comparing cerric hydrogen sulfate run at a pH of 1.3 and sodium hydrogen sulfate run at a pH of 1.0. The former had extreme catalytic action while the latter had none. This was also found to be true for the zinc fluoborate system. Fabrics impregnated with a solution at the normal pH of 3.5 and a solution which had been adjusted to a pH of 6.0 gave identical crease recovery and tensile strength.

This does not mean, however, that pH can be ignored, since strong alkalies will neutralize the catalyst being used to give either sodium fluoborate or sodium sulfate which are known to be ineffective. Fabrics to be treated should therefore have a residual alkali content of less than 0.1% or catalyst neutralization will occur.

Since zinc fluoborate has given the best results, it is being recommended for use with the epoxy resins. It has been available in the crystalline form as the hexahydrate and is now available as a 40% solution. The optimum amount to use has been determined at 7¼ parts of the hexahydrate per hundred parts of epoxy resin. This is equivalent to 12.5 parts of the 40% solution or 5 parts anhydrous. Since the hexahydrate was used in part of the work and the 40% solution in another part, all references to zinc fluoborate are based on the anhydrous material to avoid confusion.

Performance

As is the case with all crease-proofing resins, increase in resin content gives increase in crease resistance, with the first increments giving the highest proportional effect. The data shown in Figure 1 was obtained on 80 × 80 cotton print cloth impregnated with various amounts of an epoxy resin using 5 parts of (anhydrous) zinc fluoborate. The impregnated fabrics were dried for 5 min. at 90° C. and cured for 5 min. at 320° F. With about 7% add-on of resin, crease recovery is raised from about an MCRA of 81° to about 118°. At 10.5% resin add-on the slope of the curve begins to fall off slightly giving 134°. At higher resin add-on the curve approaches the maximum asymptotically, and at 21% add-on a crease recovery of 149° is obtained. The data presented here are specific, but the same type curve has been obtained on numerous occasions so it can be considered as typical performance.

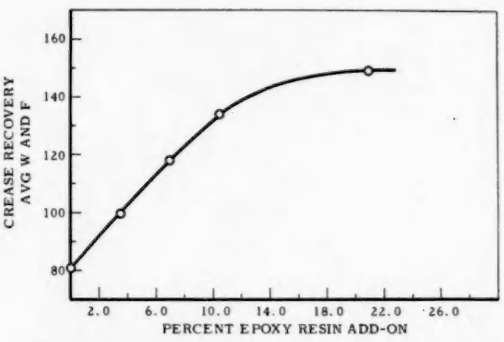


Fig. 1. Effect of epoxy resin concentration on crease resistance.

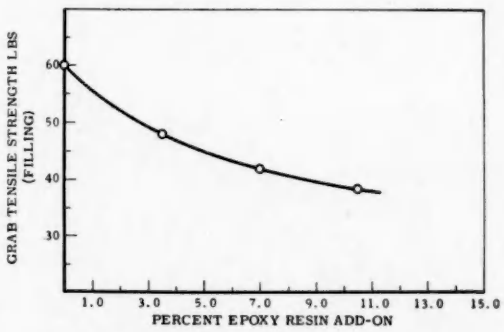


Fig. 2. Effect of epoxy resin concentration on tensile strength.

Likewise, tensile strength of the fabric is lowered as the add-on of epoxy resin is increased. Figure 2 shows tensile loss plotted against resin add-on for the same points shown in Figure 1. Small amounts of resin give quite a high strength loss in comparison to high concentrations of resin. For instance, at 3.5% resin add-on, a 20% strength loss is obtained, whereas at 10.5% resin a strength loss of 36% is obtained. Strength obtained with 21% of resin is not shown here since it was only determined once and therefore cannot be considered typical. However, in this one experiment a loss of only 33% was obtained indicating that further strength losses do not occur.

This phenomenon is further illustrated by plotting tensile strength against crease recovery (Figure 3). Usually one obtains a linear relationship between crease recovery and tensile. That is, tensile strength decreases linearly as crease recovery increases. This is not the case with epoxy-treated cotton. At low resin add-on more strength is lost than would be predicted from the gain in crease recovery. At high crease resistance, however, strength loss of epoxy-treated fabrics is the same as ethyleneurea-formaldehyde–treated fabric.

As resin add-on is increased, tensile loss becomes proportionately less in comparison to crease recovery obtained and actually flattens out giving crease recovery without appreciable loss in strength. For instance, at a crease recovery of 149° (which again is not shown) a tensile strength of 40 lb. was obtained indicating that tensile does not continue to decrease.

These data were obtained at a constant catalyst concentration of 5 phr of anhydrous zinc fluoborate (ZFB). Variation in catalyst concentration does not rectify the situation (Figure 4).

Here we have three curves obtained by padding 80 × 80 cotton with 5, 10, and 15% emulsions of epoxy resin using various concentrations of catalyst. Resin add-on amounted to 3.5, 7, and 10.5%, respectively. The 5% emulsion gives a very poor tensile to crease resistance ratio regardless of catalyst concentration, while the 15% emulsion gives the best ratio. In each case increasing catalyst concentration gives more tensile loss than crease-recovery improvement, with the worst situation being obtained for the 5% emulsion and the best situation being obtained with the 15% emulsion. The short lines intersecting the curves represent the range of catalyst concentration which gives optimum results, that is the range in which the best crease recovery can be obtained without excessive strength loss. The upper line represents 5 phr ZFB, while the lower line represents 7.5 phr ZFB. In each case, however, 7.5 phr is on the high side and it appears as though 5 phr of catalyst might be a better choice.

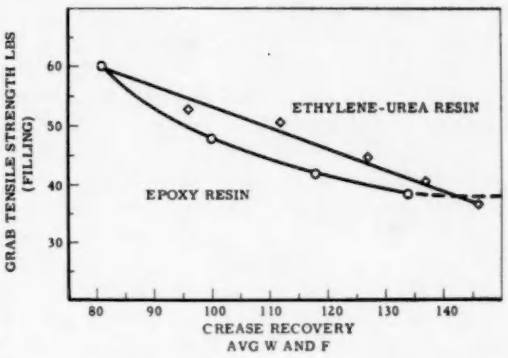


Fig. 3. Relationship of crease recovery to tensile strength.

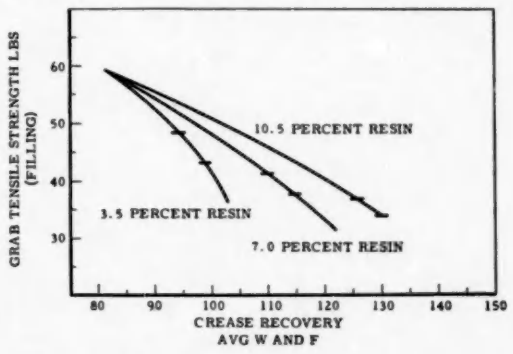


Fig. 4. Effect of catalyst concentration on crease resistance and tensile strength of fabric containing various amounts of epoxy resin.

Tear strength also decreases as crease recovery increases (Figure 5). The use of a 5% Epon emulsion lowers the tear strength of 80 × 80 fabric from a tongue tear strength of 1.4 to 1.3 lb., while 10 and 15% emulsions lower the strength to 1.1 and 0.8 lb., respectively. The addition of a softener is very effective in raising tear strength. For instance, the fabric which has been treated with 5% emulsion, containing a softener, has a tear strength of 1.5 lb. which is better than untreated fabric. The application of a 15% emulsion (giving about 10.5%

add-on) gives a tear strength of 1.1 lb. which represents only a 22% loss in tear in comparison to the 42% loss without softener. It should be noted that the softener not only raises the tear strength but also the crease angle. For instance, with 10.5% add-on crease recovery was raised from 128 to 134°.

The type of softener recommended for use with epoxy resins is an epoxidized unsaturated vegetable oil such as epoxidized soya bean oil. Twenty parts of softener per hundred parts of epoxy resin (as used to obtain these data) gives good results, although this amount may be varied to fit certain conditions. Softeners containing nitrogen should be avoided since this introduces the possibility of chlorine retention. The epoxidized oils are favored since it is felt that they are actually tied to the cellulose or to the epoxy resin giving good wash-fastness. The permanence of the softener to laundering is excellent (Table VI). An 80 × 80 print cloth treated with 10.5% of resin had an original tear strength (after an initial scour) of 1.0–1.1 lb. After 10 washings in a household automatic washing machine at 160° F. (using a built soap) the tear strength was 1.2 lb., while after 20 such washings the tear strength was still 1.2 lb. At 7.0% resin add-on the initial strength was 1.2–1.3 lb., while after 10 and 20 washings the tear strength was 1.6 and 1.4 lb., respectively. Tear strength of the original goods was 1.3 to 1.5 lb.

Tensile strength can be similarly improved by the addition of elastomeric latices. The addition of, for instance, 30 parts of Hycar 1561 per hundred parts of epoxy resin (Table VII) raises the tensile strength from 42.9 to 51.1 lb. In addition, the crease recovery was raised from 124 to 136° and the tear strength from 1.04 to 1.27 lb. The addition of larger amounts of rubber does not appear to be helpful to crease recovery or tensile strength but does seem to continue to help tear strength. At the optimum concentration of 30 phr a strength loss of only 27% occurs, whereas with no rubber a 38% loss occurs. Many elastomeric latices on the market contain anionic emulsifiers or additives which are not compatible with the epoxy resin system. Therefore, tests should be made with any latex before attempts are made to use them in production.

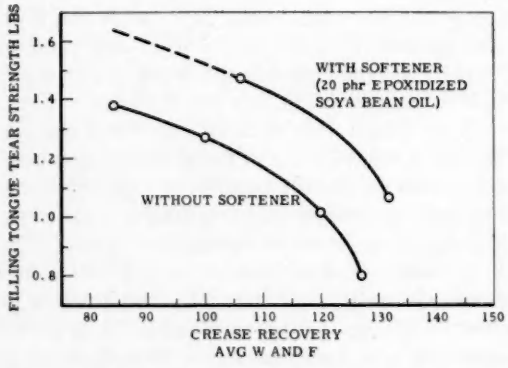


Fig. 5. Effect of softener on the tear strength and crease resistance of epoxy resin–treated fabric.

TABLE VI. Permanence of Softener to Household Laundering

Epoxy resin add-on, %	Tongue tear strength filling, lb.		
	1 Washing	10 Washings	20 Washings
10.5	1.0–1.1	1.2	1.2
7.0	1.2–1.3	1.6	1.4
0	1.3–1.5	—	—

TABLE VII. Effect of Rubber Latices on Crease Resistance and Tensile Strength of Epoxy Resin-Treated Fabric

Epoxy resin add-on, %	Hycar 1561	Crease recovery avg. W and F	Grab tensile (fill.)	Tongue tear (fill.)
8.4	0 PHR	124	42.9	1.04
8.4	20	128	47.8	1.18
8.4	30	136	51.1	1.27
8.4	40	133	45.3	1.31
8.4	50	134	52.1	1.50
0	0	94	69.9	2.39

Effect of Chlorine Bleaching

The epoxy resins are the only commercial crease-proofing agents which are truly non-chlorine-retentive either initially or after repeated alkaline washing. Fabrics treated with an epoxy resin, a melamine resin and an ethyleneurea resin (applied in the laboratory according to the manufacturer's recommendations) were given the standard AATCC chlorine test after a light scour to remove solubles and after a 1-hr. alkaline wash. After the light scour, the epoxy resin–treated cloth showed no decrease in tensile strength (Table VIII) from chlorination, whereas melamine treated fabrics showed losses of

11.9 and 13.6% and ethyleneurea–treated fabrics showed losses of 9.5 and 14.0%. After the 1-hr. alkaline wash the epoxy resin–treated fabrics showed a loss of only 2.8% in strength in comparison to 18 and 19% for melamine-treated fabrics and 50 and 74% for ethyleneurea–treated fabrics.

Durability of Epoxy Resin Finishes

The durability of epoxy resin finishes is extremely good not only toward alkaline laundering but also toward acid hydrolysis as well. This is probably due to the fact that the epoxy resins contain carbon to carbon bonds which are difficult to hydrolyze, whereas the conventional resins contain carbon to nitrogen bonds which are more readily hydrolyzed. Fabrics containing various amounts of epoxy resin were washed up to 20 times in a household automatic washer using a built soap (Table IX). After 1 wash, fabric with 10.5% add-on had a crease recovery of 132–134°. After 10 washings this was still 132°, while after 20 washings the crease angle dropped to 127°. Similarly a fabric containing 7% of epoxy resin had crease angles of 116 to 120 after 1 wash and 122 and 115 after 10 and 20 washes, respectively.

The same excellent durability is also obtained if one employs the standard cotton wash (AATCC 14–53). Fabrics containing 10.5 and 7.0% of epoxy resin were given a light scour followed by 1 and 5 cotton washes (Table X). After the light scour the fabric containing 10.5% resin had a crease angle of 132° which remained unchanged at 128 and 131° after 1 and 5 cotton washes, respectively. The fabric containing 7% of resin likewise exhibited the same durability, with crease angles of 112, 116, and 115 after 0, 1, and 5 cotton washes, respectively.

Durability toward acid hydrolysis was determined by agitating resin-treated fabric for 25 min. in 50 times their weight of 0.1*N* hydrochloric acid held at 150° F. followed by thorough rinsing and conditioning. The epoxy resin–treated fabrics had the same crease recovery after this treatment as they did before, whereas cloth treated with an ethyleneurea-formaldehyde resin lost substantially all of its crease resistance.

TABLE VIII. Effect of Chlorine Bleaching on Epoxy, Melamine, and Ethyleneurea Resin-Treated Fabrics

Resin treatment of cotton	AATCC Chlorine test % loss in strength	
	Light scour	1-Hr. alkaline wash
Epoxy, Mix 1	0.0	2.8
Epoxy, Mix 2	0.0	2.8
Melamine, No. 1	13.6	18.2
Melamine, No. 2	11.9	19.1
Ethyleneurea, No. 1	9.5	50.0
Ethyleneurea, No. 2	14.0	74.0

TABLE IX. Durability of Epoxy Resin Finish to Household Laundering

Epoxy resin add-on, %	Crease recovery, avg. W and F		
	1 Washing	10 Washings	20 Washings
10.5	132–134	132	127
7.0	116–120	122	115

TABLE X. Durability of Epoxy Resin Finish to Accelerated Washing (AATCC 14–53)

Epoxy resin add-on, %	Crease recovery, avg. W and F		
	Initial	1 Washing	5 Washings
10.5	132	128	131
7.0	112	116	115

Moisture Regain and Drying Time of Epoxy Resin–Treated Fabric

Epoxy resin–treated fabrics have a slightly lower moisture regain than untreated fabric (Figure 6) and in addition dry faster (Figure 7).

Moisture regain and drying time was carried out on 80 × 80 print cloth containing about 10.5% of

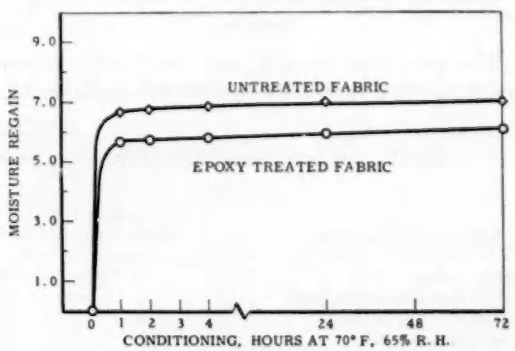


Fig. 6. Moisture regain of epoxy-treated fabric.

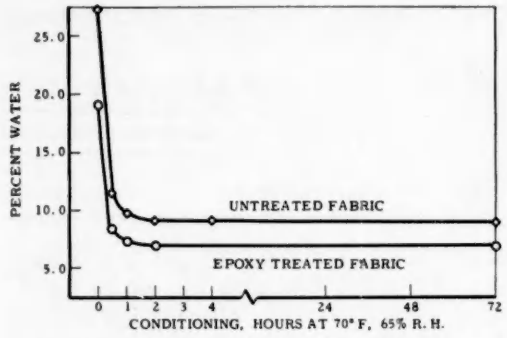


Fig. 7. Drying time of epoxy-treated fabric.

epoxy resin. As can be seen from Figure 6, the fabric containing the epoxy resin had a regain of 5.9% after conditioning for 3 hr., while the untreated control had a regain of 6.8% after this length of time showing that regain has been reduced.

Drying time was carried out using a modified version of the dynamic immersion absorption test (tentative test method 70–52) followed by conditioning at 70° F. and 65% R.H. Initial absorption for untreated fabric was 27.2% in comparison to 19.1% for the epoxy resin–treated fabric (Figure 7). In 2 hr. the untreated fabric reached practically minimum at which point it contained about 9% of water. The treated fabric reached this same point of 9% water in about 25 min. and proceeded to lose water up to 2 hr. at which point it reached practically minimum at 7% water.

These data indicate that epoxy-treated fabrics absorb less water and reach a practical "dry state" in about one-fourth the time required for untreated fabric.

Qualitative Comparison of Crease-Proofing Agents

The properties usually associated with cotton crease-proofing agents are summarized in Table XI. In this summary a figure of 4 indicates best performance while a figure of 0 indicates poorest performance. It should be emphasized that this presentation is merely a qualitative comparison and does not apply to special results obtained by some manufacturers.

The epoxy resins give slightly less crease resistance than can be obtained with either the ethyleneurea- or melamine-formaldehyde resins. Effectiveness of the epoxy resins is about equal to that obtained with the urea-formaldehyde resins. Strength loss obtained with the epoxy resins is about equal to that obtained with the urea- and ethyleneurea-formaldehyde resins and slightly lower than that obtained with the melamine-formaldehyde resins. Dimensional stability achieved is as good as that achieved with high loadings of formaldehyde but strength loss is much less. Luster of fabric treated with epoxy resins is excellent, being as good as untreated fabric in comparison to the decrease in luster obtained with other resins. In addition epoxy resins do not change the feel of the fabric in comparison to some resins which may leave the fabric harsh and boardy.

The absence of odor during processing, the absence of odor on the finished fabric, and the absence of fish odors during storage which sometimes develops with nitrogen-formaldehyde resins are also advantages in favor of the epoxy resins.

Durability of the epoxy resin finish to laundering is excellent, the fabrics retaining substantially all of their crease resistance for the life of the garments. In resistance to acid hydrolysis the epoxy resins are unique, being the only crease-proofing resins which are able to withstand acidic conditions.

Treatment with formaldehyde gives various effects depending on the amount of formaldehyde bound and the type of cure. For instance, one can achieve good dimensional stability with little crease resistance and slight strength loss. To achieve

TABLE XI. Qualitative Comparison of Properties Usually Associated with Various Cotton Crease-Proofing Agents

Crease-proofing agent	Crease resistance	Strength	Dimensional stability	Durability laundering	Resistance to acid hydrolysis	Luster
Epoxy resins	3	2–3	4	4	4	4
Ethyleneurea-formaldehyde	4	2–3	3	3	0	3
Melamine-formaldehyde	4	3	3	3	0	2
Urea-formaldehyde	3	2–3	2	0	0	2
Formaldehyde	0–4	0–2	4	4	0	4
Untreated cloth	0	4	0	—	—	4

TABLE XII. A Qualitative Comparison of the Effects of Chlorine Bleaching Produced by Various Cotton Crease-Proofing Agents

Crease-proofing agent	Effect of chlorine bleach			
	Initially	After repeated washing and bleaching	Yellowing	Scorching
Epoxy resins	4	4	4	4
Ethyleneurea-HCHO	2–3	2	4	2
Melamine-HCHO	2–3	2	0	3
Urea-HCHO	0	0	4	0
Formaldehyde	4	4	4	4
Untreated fabric	4	4	4	4

crease resistance, however, one must sacrifice most of the fabric strength.

The most outstanding property of the epoxy resins is non-chlorine-retention. A qualitative comparison of the effect of chlorine bleaching produced by various cotton crease-proofing agents illustrates the superiority of epoxy resin finishes over conventional finishes (Table XII). In the scale of 0 to 4, the higher the number the better the performance. Thus we find that epoxy resin–treated fabrics are unaffected initially while the ethyleneurea- and melamine-formaldehyde resin–treated fabrics are affected to some degree and the urea-formaldehyde resin–treated fabrics are affected to the greatest degree. The same holds true after repeated washing and bleaching except that the ethyleneurea- and melamine-formaldehyde resin–treated fabrics becomes less "chlorine resistant." The epoxy-treated fabrics do not yellow when treated with bleach as do the melamine-formaldehyde resins. Since the epoxy resins do not absorb chlorine they do not scorch after bleaching as do the nitrogen-containing resins.

Formaldehyde-treated cottons are likewise unaffected by chlorine bleaching. However, since crease resistance cannot be achieved without high losses in tensile strength, this ability of formaldehyde-treated fabrics is rather academic.

Summary

It has been shown that the epoxy resins, an entirely new class of compounds, are useful in the crease proofing of cotton. The epoxy resins give a very durable finish and treated fabrics retain substantially all of their crease resistance for the life of the garment. They are particularly suited to white goods since they are non-chlorine-retentive yielding goods which may be bleached and ironed repeatedly without loss in strength or scorching.

The chemistry of the epoxy group is discussed to show that epoxy-containing compounds do react with alcohol groups and to support the theory that cellulose cross-linking does take place.

Catalysts suitable for the use of epoxy resins in the crease proofing of cotton are listed and discussed. Of these the fluoborate salts of zinc, aluminum, and magnesium are preferred.

Data is given showing the relation of resin add-on to crease resistance, tensile strength, and tear strength and how these properties are improved by the addition of rubber latices and softeners.

Finally, the properties obtained with the epoxy resins were qualitatively compared with those usually associated with other crease-proofing agents.

Acknowledgments

The authors acknowledge the assistance received from their co-workers, Mr. N. E. Burrin and Mrs. N. P. Dill.

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The Mechanism of Crease Resistance Development on Cellulosic Fabrics Treated with Dimethylol Ethylene Urea[1]

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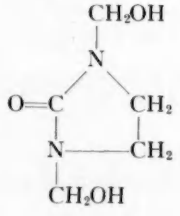
PROBABLY the most significant and important development in the finishing of textiles in the post-war era has been the chemical modification of cotton to give greatly improved resilience and dimensional stabilization. By combining the chemical treatments with fabric calendering operations, the textile finishing industry has also achieved durable surface glazes and embossed effects on cotton. One of the most effective chemical compositions used in achieving these desirable modifications is dimethylol ethylene urea (DMEU).

Dimethylol ethylene urea finishes have proved particularly satisfactory because of their crease-resistant properties, minimal chlorine retention, lack of surface resin formation, and durability to extended laundering in detergent solutions. DMEU itself is very stable and may be kept for years under ordinary conditions of storage. Thermosetting resins of the urea-formaldehyde types are relatively deficient in all of these important properties.



(1)

Dimethylol ethylene urea (1), or more precisely 1,3-bis(hydroxymethyl)-2-imidazolidone, is bifunctional and contains no hydrogen-bearing nitrogen atoms. These two characteristics are responsible in part for the differences in behavior between DMEU and the urea-formaldehyde (UF) or melamine-formaldehyde (MF) resins on application to cellulose.

[1] Contribution No. 221 from Jackson Laboratory.

The desirable combination of properties exhibited by DMEU makes it particularly suitable for use in producing the so-called "wash and wear" finishes which are enjoying current popularity. Two recent papers [9, 12] published in the *American Dyestuff Reporter* discuss these finishes in detail. This work showed that DMEU was superior to both the UF and MF resin types in producing wash and wear finishes.

Wash and wear finishes do not differ fundamentally from the conventional crease-resistant finishes. In wash and wear finishes greater care must be exercised in the selection of proper fabric constructions and print patterns. In addition, higher concentrations of DMEU generally are employed in wash and wear finishes, and auxiliary agents are often added to provide greater fiber-to-fiber lubricity and water resistance.

DMEU is applied to cotton fabrics by conventional pad-dry-cure procedures. An acidic catalyst such as tartaric acid is required to achieve fixation. Latent acid catalysts such as certain alkanol-amine hydrochlorides and magnesium chloride also are used widely.

The two most important improvements in fabric properties are dimensional stabilization to washing and greater crease-angle recovery. The improvement in these properties is illustrated by the data in Table I.

DMEU and the UF or MF thermosetting resins exert their beneficial effects by increasing the modulus of elasticity and elastic recovery. An increase in fiber stiffness also occurs, but the best finishes do not increase the yarn or fabric stiffness. Fiber extensibility and swelling in water are decreased. The modified cellulose fibers are no longer soluble in cuprammonium hydroxide, as is untreated cellulose.

The effect of DMEU concentration on the load-

TABLE I. Effect of DMEU on Crease-Angle Recovery and Dimensional Stabilization Properties

Cotton, 80×80	Monsanto Wrinkle Recovery Test (deg.) [2]		Shrinkage (40 min. in soap solution, 80° to 100° C., wash wheel) [1]	
	Warp	Fill	Warp	Fill
4% DMEU	122	127	0.6%	0.6%
Untreated	56	62	5.4%	2.8%

elongation properties of rayon is illustrated in Figure 1.

Figure 1 illustrates how the application of DMEU to cellulose causes substantially greater resistance to elongation under stress. This increase in the modulus of elasticity was observed for both rayon and cotton.

The effects of UF and MF resins applied to cellulose have been studied in detail [5, 7]. Studies conducted at the Jackson Laboratory of the Du Pont Company have shown that DMEU and the UF or MF resins cause basic modifications in fiber and fabric character in much the same manner.

The location of fixed DMEU in cellulose was investigated by using dye staining techniques. Certain organic dyes that are ordinarily not substantive to cellulosic fibers are absorbed when the fiber is modified by application of DMEU or thermosetting resins. The depth of shade of the absorbed dye will

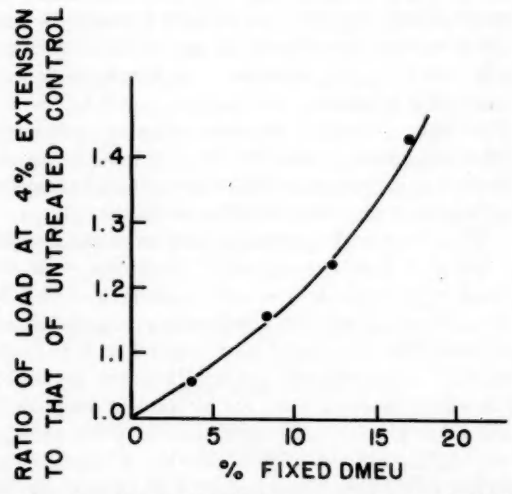


Fig. 1. Effect of DMEU concentration on the load-elongation properties of rayon yarn (from treated rayon satin-warp yarn, 150 den., 40 filament).

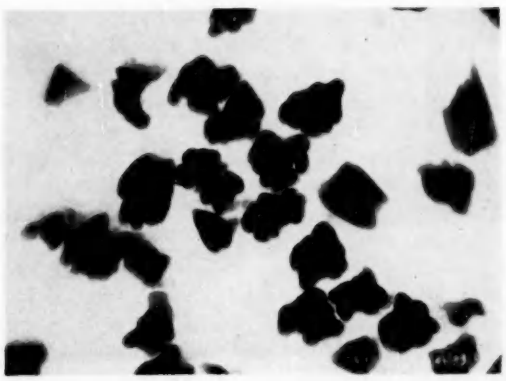


Fig. 2. Cross section of rayon fibers treated with DMEU from water solution and stained with Tollens' reagent.

then indicate the amount of DMEU fixed at different locations within the fibers. Microscopic examination of fiber cross sections shows that the DMEU is uniformly deposited throughout the fiber structure.

The most useful staining technique, however, was not based on preferential dye absorption but on the localized reduction of Tollens' reagent by the fixed DMEU. Cross sections of fibers containing fixed DMEU were treated with a solution of ammonical silver nitrate. After exposure to this solution for ½ hr. in the dark, the sample was rinsed and treated with sodium thiosulfate solution to remove excess silver ion. Using this procedure, a black deposit of silver was found within the fiber where the fixed DMEU was deposited. This procedure was first described by Bermesser in 1948 as a test for the location of thermosetting resins on rayon fabric [3].

DMEU, when applied by conventional means from water solution, shows a uniform deposit of silver throughout the fiber, as illustrated by the photomicrograph (Figure 2). When the DMEU is applied from alcohol solution, however, poor penetration of the fiber is obtained, as indicated by the deposition of silver on the periphery of the fiber (Figure 3).

Application of DMEU from alcohol gives excessive fabric stiffness and very poor crease recovery. When DMEU is applied from water, however, a resilient fabric with a soft hand is obtained. DMEU applied from alcohol is similar to the UF and MF resins in that these resins may prepolymerize to such an extent that they cannot penetrate the fiber. When prepolymerization occurs, resin will be found on the surface of the fibers. Fabrics so treated may be

Fig. 3. Cross section of rayon fibers treated with DMEU from alcohol solution and stained with Tollens' reagent.

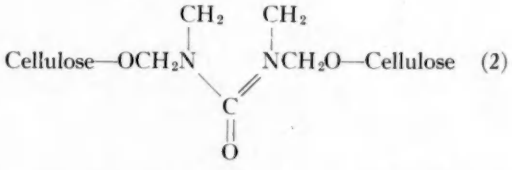
somewhat harsh in hand and tend to dust off resin particles on flexing.

Most workers who have studied the application of UF and MF resins to cellulosic fabrics have concluded that a covalent bond is formed on curing between the resin and the cellulose [4 through 6, 11]. Conversely, Landells [8] and Marsh [10] are of the opinion that chemical reaction between UF resin and cellulose does not occur. They believe that the formation of a resin polymerizate within the interstices of the fiber is sufficient to explain the crease recovery and the other properties that result. Since both UF and MU resins polymerize in the presence of acid to give water-insoluble products, such an explanation would appear to be plausible. Polymerized DMEU is water-soluble, and therefore it is not possible to attribute the modifications in fiber properties to mechanical restraint.

DMEU treated with such catalysts as diammonium phosphate, magnesium chloride, or tartaric acid, at 160° C. for 10 to 30 min., gives a glassy polymer which is soluble in water. Obviously, therefore, an explanation of crease resistance development, based on the formation of a durable, water-insoluble polymer within the pores of the fiber, is not tenable. This difference in behavior between DMEU and the UF and MF resins can be attributed to the bifunctional nature of DMEU. The UF and MF resins are polyfunctional in nature and can cross-link readily with themselves to give insoluble resins of high molecular weight.

Our work with DMEU suggests that covalent bonds are formed and that these bonds are formed in such a manner that the cellulose chains are cross-linked.

In the presence of cellulose, the same curing and catalyst conditions as described above will cause DMEU to produce a durable, water-insoluble, and hence nonextractable finish. Analogous results are obtained when DMEU is cured in the presence of polyvinyl alcohol (PVA). In this instance neither of the reactants (DMEU or PVA) is insolubilized when treated separately with heat and acid. The combination of the two materials, however, results in the formation of a completely water- and alkali-insoluble product. These simple observations on water solubility comprise strong evidence that a chemical bond is formed between DMEU and the hydroxyl groups of the cellulose. The covalent bond formed on curing is probably a methylol ether, as shown by structure 2.



(2)

Chemically, ethers exhibit good stability to alkaline solutions but are much more readily attacked by acids. This same relative stability is also characteristic of DMEU-cotton finishes. They are resistant to alkalies, such as soda ash, even at boiling temperatures, but they are attacked readily by hot dilute acids with removal of the DMEU and regeneration of the cellulose in a substantially unchanged condition.

Structure 2 depicts the cross-linking of polymeric cellulosic chains by the DMEU. Evidence for cross-linking is demonstrated by treatment of cellulosics with other mono- and bifunctional compounds.

Monofunctional compounds, such as monomethylol formamide and monomethylol acetamide, can be fixed on cellulose in the same manner as DMEU. The fact that these two compounds are insolubilized indicates that they must have reacted with the cellulose. The methylene-bis-amides which could be formed by dimerization of the monomeric compounds are water-soluble. Although these two monomethylol amides are insolubilized on the cellulose, they do not confer any crease recovery properties nor do they bring about insolubility of the cellulose in cuprammonium hydroxide. The probable structures

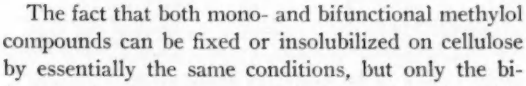
of the reactant products with cellulose are illustrated by (3) and (4).

(3)

(4)

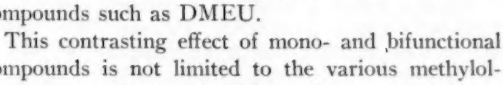
The fact that both mono- and bifunctional methylol compounds can be fixed or insolubilized on cellulose by essentially the same conditions, but only the bifunctional methylol compounds impart the desirable mechanical properties, provides strong evidence for cross-link formation on application of bifunctional compounds such as DMEU.

This contrasting effect of mono- and bifunctional compounds is not limited to the various methylol-type compounds that have been discussed. For example, phenyl isocyanate will react with dry cellulose in dry dimethyl formamide solvent to give a durable chemically linked derivative. The mechanism involved is probably the reaction of the cellulose hydroxyl groups with the isocyanate to give a phenyl carbamate (5).



(5)

Cotton fabric treated with phenyl isocyanate does not become insoluble in cuprammonium hydroxide or show any significant improvement in crease-resistant properties. Diisocyanates, on the other hand, such as toluene-2,4-diisocyanate and hexamethylene diisocyanate, react under the same conditions to give fabrics showing cuprammonium-hydroxide insolubility and substantially improved crease recovery properties. The crosslinked structure obtained is probably as shown by (6).



(6)

Summary and Conclusions

1. Dimethylol ethylene urea reacts with cellulosic fabrics at elevated temperatures in the presence of acids to give improved physical properties such as crease recovery and dimensional stabilization.

2. The fixation of DMEU on cellulose results in an increase in the modulus of elasticity, a lower degree of swelling in water, and insolubility in cuprammonium hydroxide solution.

3. Staining studies with Tollens' reagent have shown that DMEU, applied from water solution, is deposited uniformly throughout the individual cellulosic fibers. There is no surface deposition of the DMEU.

4. DMEU, itself, is not converted to water-insoluble products by heat curing in the presence of acids; therefore, the laundering durability of DMEU finishes on cellulose cannot be attributed to the interstitial deposition of polymerized resin within the cellulosic fiber. The durability of the fixed DMEU and the resulting modifications in fiber and fabric properties can be explained only by a chemical interaction of the DMEU and cellulose.

5. The chemical linkages of DMEU to cellulose, probably methylol ethers, are formed in such a manner that cross-linking of cellulosic chains occurs. The evidence for cross-linking was obtained by contrasting the effects obtained on fixing mono- and bifunctional compounds on cellulose. It is this cross-linking by DMEU, rather than substitution of individual hydroxyl groups, that is responsible for the improved mechanical properties of cellulose.

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Comparison of Wrinkle-Resistant Finishes for Cotton

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Abstract

A brief discussion is given on the mechanism by which wrinkle-resistant properties are imparted to cotton fabrics by the use of urea- and melamine-type resins. A summary of the chemistry of these products is given. The results of an extensive study of the application of urea, modified urea (ethylene urea), melamine, and modified melamine formaldehyde resins using ammonium, alkanolamine, and metallic inorganic salt accelerators to cotton fabric are presented. The effect of variations in resin concentration, curing temperature, and time on the wrinkle recovery, tensile strength, tear strength, and discoloration of the treated fabric before and after washing is discussed. This work was designed and analyzed statistically to ensure an accurate and authoritative presentation of the more important properties imparted to cotton fabric for the systems studied. These data should enable a cotton fabric finisher to select the optimum resins and conditions of application to obtain the wrinkle-resistant finish best suited for the specific fabric properties desired.

HISTORICALLY, wrinkle-resistant finishes on cellulosic fabrics [8] had their start with the use of urea formaldehyde and an acid-forming ammonium salt accelerator. The early work was primarily on rayon fabrics. The second important development in the wrinkle-resistant field was the application of melamine formaldehyde to both rayon and cotton. Next came the use of the alkanolamine salt accelerators followed by the modified urea formaldehyde (ethylene urea formaldehyde). The more recent developments of importance are metallic salt accelerators and the modified melamine formaldehyde.

A number of papers have been written on the properties of the finishes obtained on cotton fabrics using these different products; however, no really comprehensive comparison of them has been made so that the finisher can choose the particular system best designed for the specific fabric properties desired. The work described in this paper was carried out to make such data available.

In order to have a better understanding of wrinkle-resistant finishes, let us briefly review the chemistry of urea and melamine formaldehyde and possible mechanisms for explaining how wrinkle resistance is obtained.

Urea and melamine formaldehyde used for imparting wrinkle resistance to cellulosic fabrics have been termed "thermosetting resins." Ethylene urea formaldehyde has been called both a "resin" and a "cellulose reactant." Actually, in the form used for wrinkle-resistant finishes, these products are not resins but chiefly monomeric chemicals capable of both resin formation and reaction with cellulose.

Urea formaldehyde (dimethylol urea) is tetrafunctional—has four reactive positions (the two hydroxyl groups and the two hydrogens attached to the two nitrogen groups), as shown in Figure 1. Melamine formaldehyde (trimethylol melamine is hexafunctional—has six reactive positions (the three hydroxyl groups and the three hydrogens attached to the amino nitrogens), as shown in Figure 2. Ethylene urea formaldehyde is difunctional—has two reactive groups (the two hydroxyl groups), as shown in Figure 3. An ethylene urea formaldehyde linear polymer is shown in Figure 4. Such a polymer was formed in our laboratory by merely heating monomeric ethylene urea formaldehyde at 130°–135° C.

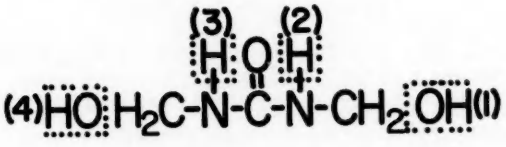

Fig. 1. Structural formula for urea formaldehyde.

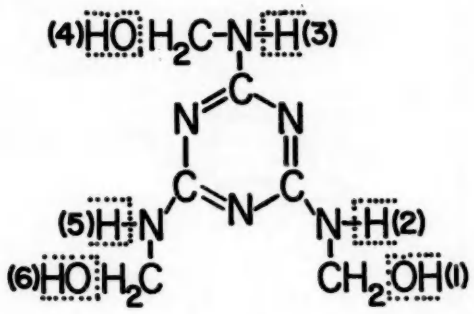

Fig. 2. Structural formula for melamine formaldehyde.

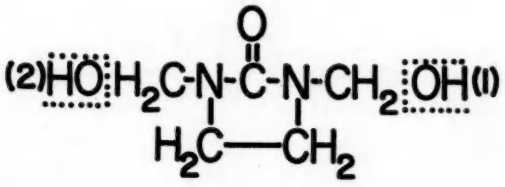

Fig. 3. Structural formula for ethylene urea formaldehyde.

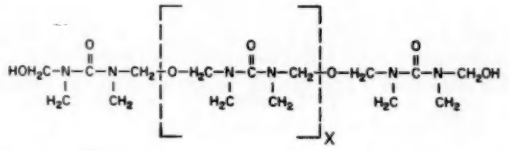

Fig. 4. Structural formula for ethylene urea formaldehyde polymer.

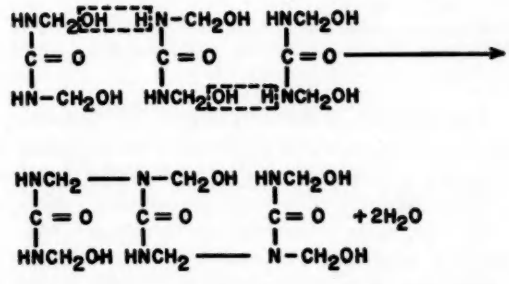

Fig. 5. Formation of urea formaldehyde polymer, linear type.

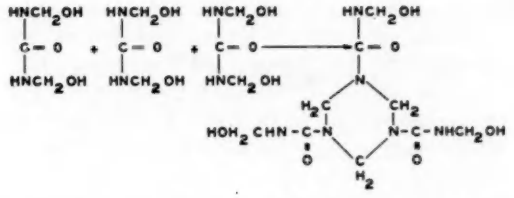

Fig. 6. Formation of urea formaldehyde polymer, cyclic type.

(No accelerator was used since it would interfere with the subsequent molecular weight determination made on the product.) In 4 hr. a product with an average molecular weight of 2500, corresponding to a linear polymer averaging 17 units long, was formed.

Two ways that monomeric urea formaldehyde can condense with itself to form polymers [9] are shown in the next two figures. Three molecules of dimethylol urea are pictured in Figure 5 as condensing to form a linear trimer. This condensation reaction can, of course, continue in the same manner to form a chain polymer. Three molecules of dimethylol urea are shown condensing to form a ring trimer in Figure 6. Further condensation in this manner is, of course, possible with the formation of a polymer of ring trimers. It can be seen that polymers of a variety of structures are possible with the condensation of urea formaldehyde monomers to form chain or ring polymers or combinations of the two. Similar chain and ring polymers [9] can be formed from melamine formaldehyde monomers, as shown in Figures 7 and 8, respectively.

Melamine, urea and ethylene urea formaldehyde can react through the methylol group with a hydroxy group of cellulose by means of an ether linkage [2]. Infrared spectra of melamine formaldehyde–treated cellophane films have indicated that such a chemical reaction may occur [2, 5]. It has been postulated that the "resin" molecules or "reactants" cross-link adjacent cellulose chains in the amorphous regions within a cotton fiber [1, 2, 3]. Figure 9 pictures such a cross-linking.

Although it is conceivable that wrinkle resistance could be obtained as the result of resin formation within the cotton fiber, it is believed that it primarily results from cross-linking between adjacent cellulose chains [1, 2, 3]. Such a cross-linking process would tend to prevent the cellulose chains

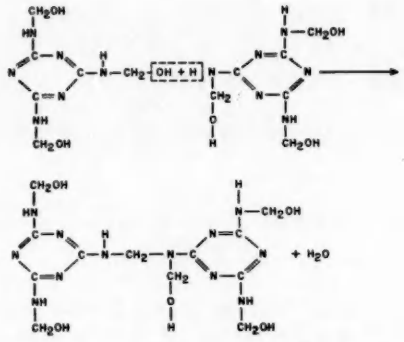

Fig. 7. Formation of melamine formaldehyde polymer, linear type.

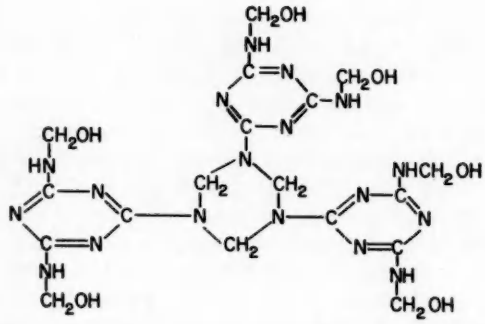

Fig. 8. Structural formula for melamine formaldehyde polymer, cyclic type.

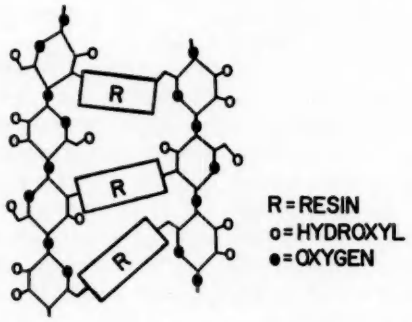

Fig. 9. Cross-linking of resins to cellulose.

from slipping irreversibly past one another under the influence of an applied stress. The prevention of this irreversible slippage reduces the permanent set of a cellulosic fiber, thereby increasing its elasticity and imparting wrinkle resistance [2]. This increase in elasticity of the fiber is carried through to the fabric, as shown in Figure 10, which gives the load extension curves for the untreated and urea formaldehyde counterparts [2].

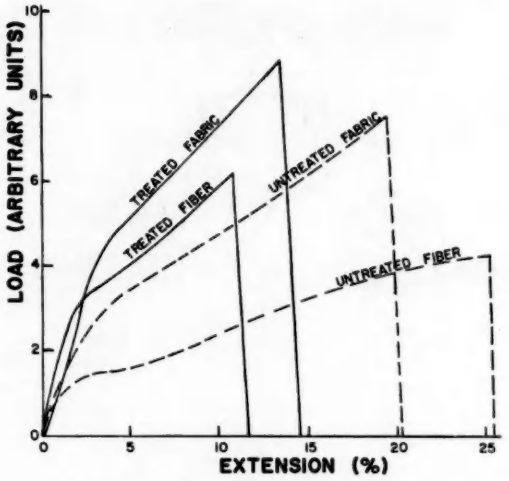

Fig. 10. Stress-strain curves for treated and untreated rayon fiber and fabric.

The resins studied included the most extensively used types. The concentration of these products applied to the fabric was varied over a wide range to include not only the normally used concentrations but also lower and higher solids as well, as shown in Table I.

TABLE I. "Resins" Studied

Resin	Designation	% on wt. of fabric
Urea formaldehyde	UF	4–20
Ethylene urea formaldehyde	EU	2–11
Melamine formaldehyde	MF	2–11
Modified melamine formaldehyde	Modified MF	2–11

The accelerators studied included the most extensively used types. The accelerators were applied at those concentrations generally found to give optimum wrinkle recovery values, as shown in Table II. (All accelerator concentrations are expressed in terms of active ingredients.)

Each resin was applied with each of the accelerators, giving a total of twelve resin accelerator systems studied. The resins were applied to bleached,

TABLE II. Accelerators Studied

Accelerator	Chemical composition	% on resin solids
Ammonium salt	Ammonium sulphate	3.5
Alkanolamine salt	2-amino-2-methyl propanol-1 hydrochloride	7
Metallic inorganic salt	Magnesium chloride	12

unmercerized, 80 × 80 cotton. The untreated fabric had a pH value of 6.8 The treated fabric was dried and then cured at temperatures ranging from 275° to 365° F. at times varying from 0.75 to 8.25 min. This range of time and temperature of cure was chosen to represent not only those conditions usually considered optimum but also conditions of less as well as more cure.

The data used in this paper were obtained by statistical means. The actual experiments were statistically designed to afford maximum efficiency for every individual experiment as well as to ensure the most accurate, precise, and unbiased data. The design was of such a nature as to exclude errors which are normally encountered in experimental work. Some of the errors which were eliminated by a canceling-out effect are the errors due to differences in the physical properties of the fabric used for treatment; variations in processing equipment from day to day; fluctuation in apparatus as well as differences between operators used in the application and the testing of the treated fabrics.

At the start of the experimentation it was necessary to evaluate the physical properties of cloth samples taken from approximately 2 miles of 80 × 80 cotton fabric in order to obtain 0.7 mile of fabric, the physical properties of which were closely similar. The 0.7 mile of fabric was divided into 216 individual lengths to receive 216 resin treatments.

The treated fabric was tested for the properties shown in Table III.

TABLE III. Fabric Properties Studied

Wrinkle recovery (CCC-T-191b, method 5212)
Tensile strength (CCC-T-191b, method 5100)
Tear strength (Elmendorf) (CCC-T-191b, method 5132)
Discoloration due to curing
Yellowing due to chlorine bleaching

The wrinkle recovery, tensile strength, and discoloration properties were evaluated after a process wash and after a number of washes in a Najort washing machine at a temperature of 140° F. using 0.1% neutral soap and 0.02% available chlorine.

The data were then collected and subjected to a statistical analysis. The analysis for the most part was carried out on a high-speed electronic computer which utilized over 300 sq. ft. of paper to record the resulting relationships between the variables under investigation and the physical properties obtained. It is estimated that the calculations would have required 20 years for one man had not the electronic computer been available.

In all cases, mathematical relationships were found to exist between the many physical properties tested and the variables of resin concentration, time of cure, and temperature of cure. A high statistical confidence in these relationships was realized because of the small fluctuations between the many control points which were randomly scattered throughout the 216 trials. Thus, it is possible to accurately compare the physical properties of the different resin-accelerator systems.

Ordinarily one can show a relationship between one independent variable and a dependent variable by means of a graph of the two variables. Three variables can be included in a similar graph, in which the ordinate represents one variable, the abscissa a second variable, and the third variable is plotted against the other two variables using lines of equal value. In this particular investigation, three varia-

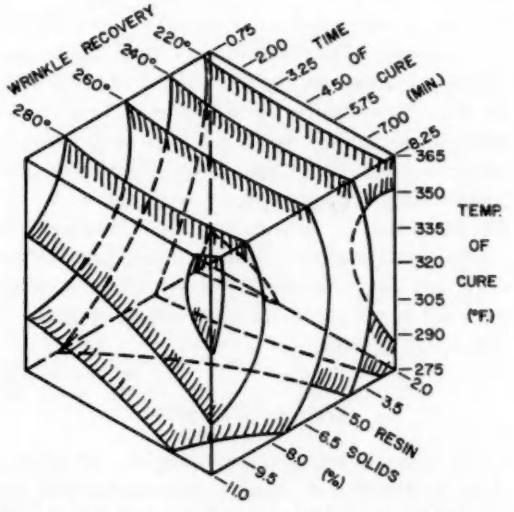

Fig. 11. Diagram of a three-dimensional model of relationship between processing variables and wrinkle recovery.

bles were studied, and in order to graphically show the relationship between the three variables and a physical property such as wrinkle recovery, it was necessary to use a three-dimensional model. Figure 11 is a diagram of such a model—a cube in which the axes represent the three variables. The modified MF resin and alkanolamine hydrochloride accelerator system is presented in this three-dimensional model. The time of cure is represented by planes parallel to the front of the cube; the temperature of cure is plotted as planes parallel to the base of the cube; and the resin concentration is represented by planes parallel to the sides of the cube. The curvilinear surfaces represented by slices through the cube have equal wrinkle recovery values. In other words all points on each one of these surfaces have the same wrinkle recovery values (warp plus fill) showing that a given wrinkle recovery can be obtained by a combination of many different time, temperature, and resin concentration relationships. Some of the important relationships are readily apparent. For example, the wrinkle recovery increases as the resin concentration increases. The wrinkle recovery in general increases as the time of cure increases and as the temperature of cure increases. There are exceptions to these generalities for this particular system. A study of the top face of the cube, which represents the condition where the curing temperature is held constant at 365° F. while the resin concentration and time of cure are varied, shows that the wrinkle recovery is not appreciably affected by variations in the time of cure since the wrinkle recovery lines on this face are almost straight while the time of cure varies from 0.75 to 8.25 min. This unusual relationship would not have been found by conventional studies of such a system. Similar cubes representing wrinkle recovery could be drawn for the additional 11 systems studied. However, the results will be plotted in two dimensional graphs since they are more readily understandable. Only the most important of the vast volume of data collected will be shown.

Wrinkle Recovery

The effect of resin concentration on the wrinkle recovery imparted by various resin-accelerator systems is shown in Figure 12 (*a*, *b*, and *c*). In this figure, the curing conditions are held constant at 1.5

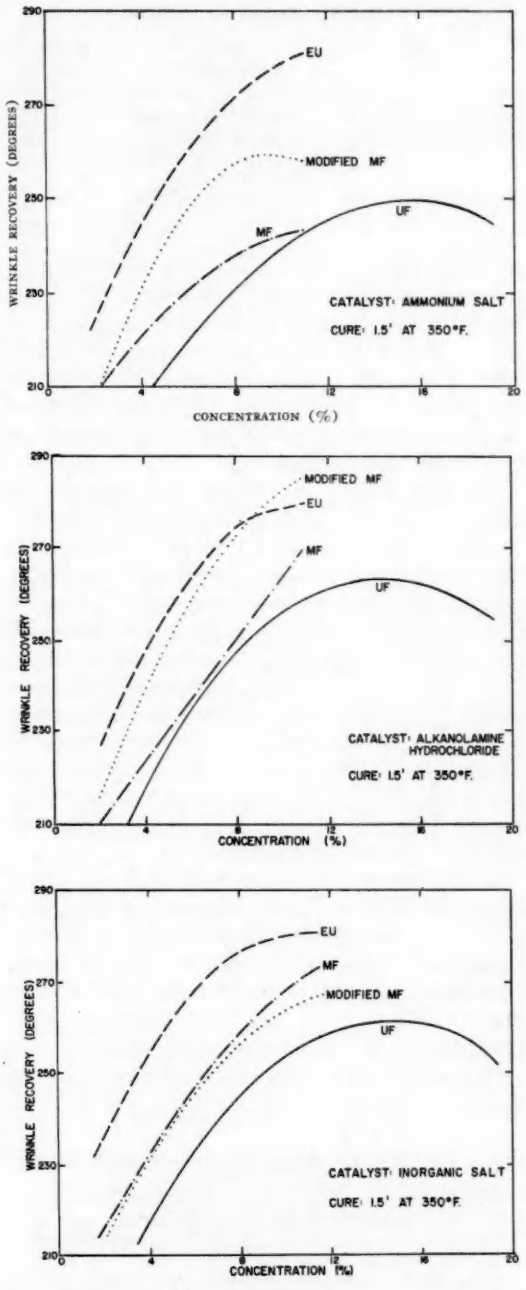

Fig. 12. Effect of resin concentration on wrinkle recovery imparted by various resin-accelerator systems. *a*. Using ammonium salt as accelerator. *b*. Using alkanolamine hydrochloride as accelerator. *c*. Using metallic inorganic salt as accelerator.

min. at 350° F. The effect of accelerator on the wrinkle recovery is shown to be as follows:

1. The ammonium salt gives the lowest wrinkle recovery values for each resin.

2. The metallic inorganic salt is the most efficient for the MF.

3. The alkanolamine hydrochloride is the most efficient for the Modified MF.

4. All three accelerators are effective for EU with the alkanolamine hydrochloride being slightly better than the ammonium salt, while the metallic inorganic salt is slightly superior to the alkanolamine hydrochloride.

These data show that EU gives the highest wrinkle recovery and UF gives the lowest wrinkle recovery. The wrinkle recovery values with UF reach a maximum at 12–15% solids and then decrease. This decrease is propably due to the increase in the stiffness of the fabric at the very high concentrations of resins.

The melamine resins give intermediate wrinkle recovery values. When the alkanolamine hydrochloride accelerator is used with the modified MF, however, essentially the same wrinkle recovery is obtained as found with the EU.

There are four possible explanations for the difference in wrinkle recovery values obtained for a given weight concentration of resin.

1. The relative amounts of resin inside the fiber and outside the fiber caused by differences in size of the resin molecules.

2. The difference in the molecular weight of the monomers.

3. The amount of resin polymerized within the fiber compared with that reacted with the cellulose.

4. The difference in the length of cross-link between adjacent cellulose chains.

It is not believed that reason 1 is the important factor since all four resins are chiefly monomeric. The monomeric molecules are sufficiently small to enter the fiber if we accept gas absorption measurements of the pore size of cotton fibers [4]. Wrinkle recovery plots based on concentration of molecules containing two or more methylol groups, rather than weight concentration, indicate that factor 2, is the most important one. Figure 13 gives such a plot for all four resins cured at 1.5 min. at 350° F., using a metallic inorganic salt accelerator. The fact that the curves for all four resins make up essentially one curve shows that equal wrinkle recovery is obtained with the concept that wrinkle recovery is obtained more methylol groups. These data are in keeping for the same concentration of molecules with two or through the cross-linking of adjacent cellulosic chains.

The wrinkle recovery obtained with the different resin–accelerator systems varies with the curing conditions. There are three ways in which the wrinkle recovery can respond to changing curing conditions. Figure 14, which represents the modified MF–ammonium salt system, shows that the wrinkle recovery increases as the time or temperature of curing increases. Figure 15, which pictures the EU–alkanolamine hydrochloride system, shows that the wrinkle recovery can be practically unaffected by varying the curing conditions. A third possibility is illustrated in Figure 16, which shows the EU–ammonium salt system. Here the wrinkle recovery value increases to a maximum as the temperature increases to 320° F. By increasing the curing temperature above 320° F., lower wrinkle recovery values are obtained. The lower wrinkle recovery at the higher curing temperature is probably due to hydrolysis of the resin through overcuring. Nitrogen determinations of the process-washed treated cloth support this idea; the nitrogen content of the fabric cured at 365° F., being less than that of the fabric cured at 320° F.

The effect of curing conditions on the wrinkle recovery obtained with 5% resin solids in each of the 12 systems studied is summarized in Figures 17 through 20.

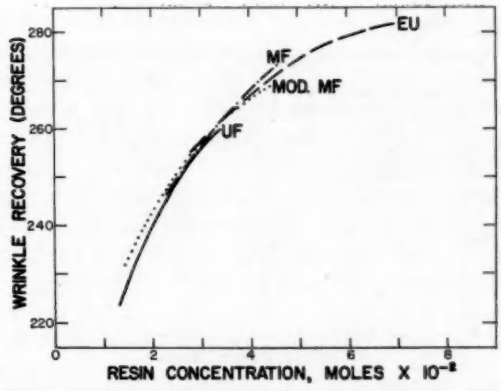

Fig. 13. Relationship of molecular concentration to wrinkle recovery.

The MF systems are shown in Figure 17. The area between the like curves represents the range of wrinkle recovery obtained within the curing conditions studied for each accelerator. The metallic inorganic salt gives the highest wrinkle recovery and the ammonium salt gives the lowest wrinkle recovery, but there is much overlapping of the areas. For wrinkle recovery values of 200°–225°, for example, any of the accelerators can be used, the choice being dictated by the effect of the accelerator on other fabric properties or economics.

In Figure 18, the EU systems are summarized. The ammonium salt generally gives the poorest wrinkle recovery and the area covered by this accelerator does not overlap the areas of the other accelerators to any great extent. The alkanolamine hydrochloride and metallic inorganic salt give substantially the same wrinkle recoveries. These wrinkle recovery values are quite high, about 250°–265°. The time and temperature of cure have little effect on the wrinkle recovery obtained with either the alkanolamine hydrochloride or the metallic inorganic

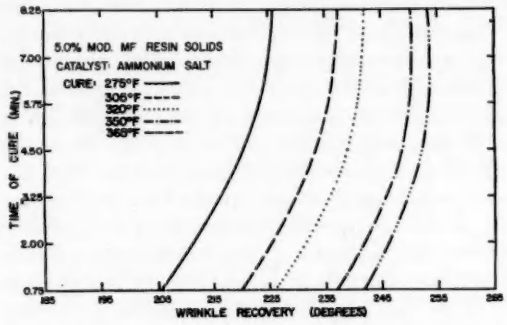

Fig. 14. Effect of curing conditions on wrinkle recovery, using modified melamine formaldehyde-ammonium salt system.

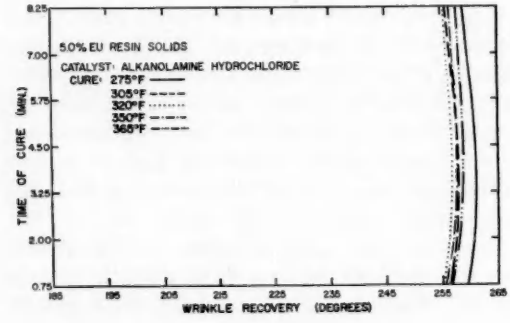

Fig. 15. Effect of curing conditions on wrinkle recovery, using ethylene urea formaldehyde-alkanolamine hydrochloride system.

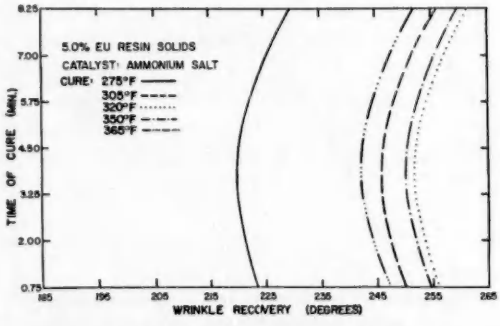

Fig. 16. Effect of curing conditions on wrinkle recovery, using ethylene urea formaldehyde-ammonium salt system.

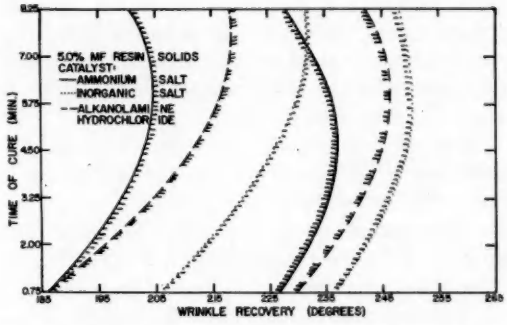

Fig. 17. Effect of curing conditions on wrinkle recovery, using various accelerators with melamine formaldehyde.

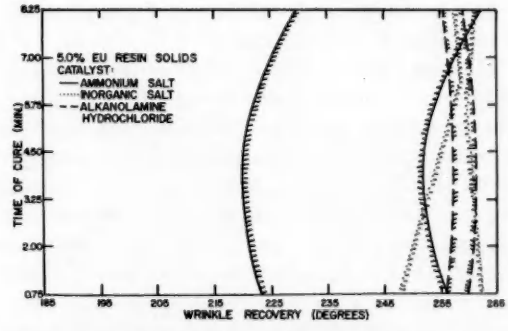

Fig. 18. Effect of curing conditions on wrinkle recovery, using various accelerators with ethylene urea formaldehyde.

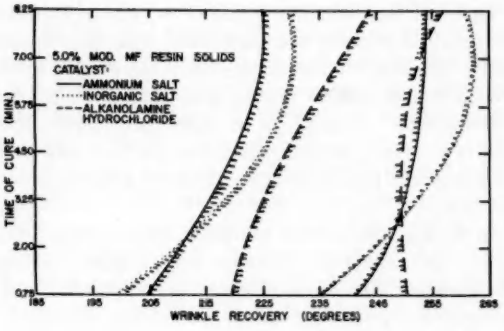

Fig. 19. Effect of curing conditions on wrinkle recovery, using various accelerators with modified melamine formaldehyde.

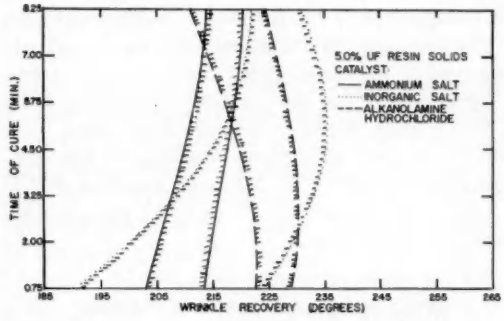

Fig. 20. Effect of curing conditions on wrinkle recovery, using various accelerators with urea formaldehyde.

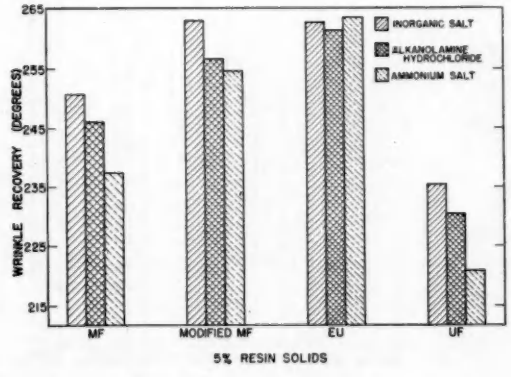

Fig. 21. Maximum wrinkle recovery obtained with resin-accelerator systems.

salt. The time of cure has little effect on the wrinkle recovery obtained with the ammonium salt, but the temperature is important, as is shown in Figure 16. These data indicate that with the metallic inorganic salt and alkanolamine hydrochloride, the time and temperature of cure of the EU do not have to be controlled within narrow limits for optimum wrinkle recovery.

In Figure 19, the wrinkle recovery obtained with 5% of modified MF is shown. Although there is considerable overlapping of the areas produced by the various accelerators, the metallic inorganic salt accelerator gives the highest wrinkle recovery values at long times of cure. These data appear to be in sharp contrast to the data for a 1.5-min. cure at 350° F. given previously, which showed that alkanolamine hydrochloride gave higher wrinkle recovery than the other accelerators. However, it can be seen that in Figure 19, also at short times of cure, the alkanolamine hydrochloride gives the best results.

In Figure 20 the wrinkle recovery values of cotton fabric treated with 5% UF is shown. The metallic inorganic salt curves generally overlap the others. Again the ammonium salt generally gives the poorest wrinkle recovery and the metallic inorganic salt gives the highest wrinkle recovery under most conditions.

The maximum wrinkle recovery obtained with a given resin and accelerator combination at 5% solids was read from Figures 17 to 20 and shown in bar graphs in Figure 21. This summary shows that the metallic inorganic salt gives a wrinkle recovery value equal to or greater than that obtained with the other accelerators with all four resins. The ammonium salt accelerator gives the lowest wrinkle recovery for all the resins except for EU where it is equal to that obtained with the metallic inorganic salt. The modified MF and EU resins give the highest wrinkle recovery while the UF gives the lowest wrinkle recovery. In interpreting the data in Figure 21, one must be careful. The maximum wrinkle recovery may have been obtained, but other fabric properties such as the color, for example, may be unsatisfactory, as will be shown with subsequent data.

Figure 22 (*a*, *b*, and *c*) shows the durability of wrinkle recovery to repeated washes in a Najort washing machine at 140° F., using 0.1% neutral soap and 0.02% active chlorine.

These graphs show that in general the melamine resins have greater durability than the ureas.

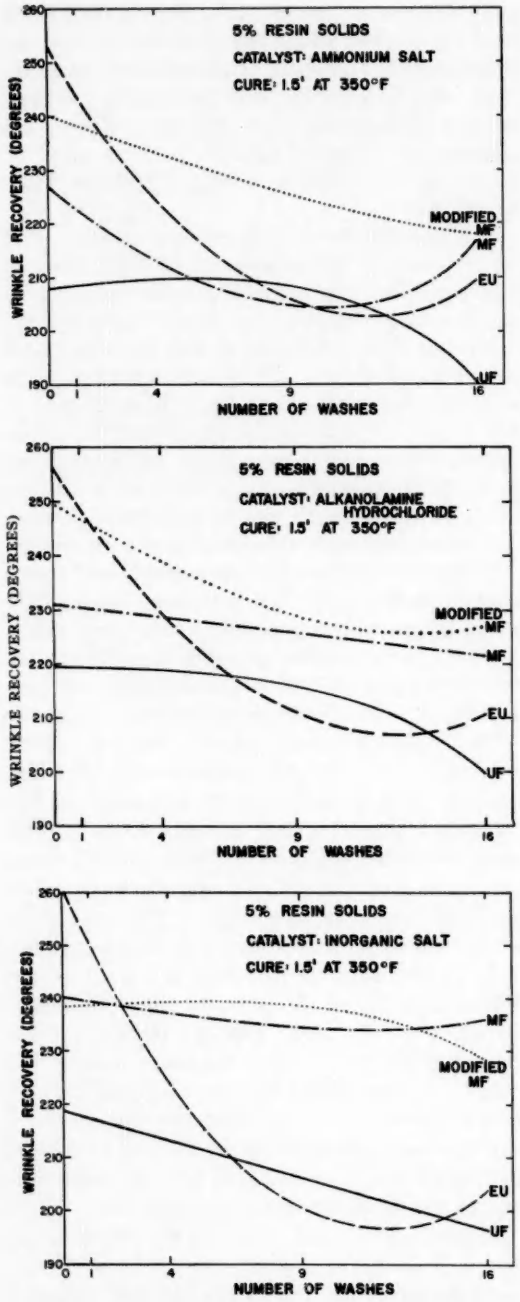

Fig. 22. Durability of wrinkle recovery to chlorine washing. *a.* Using ammonium salt accelerator. *b.* Using alkanolamine hydrochloride accelerator. *c.* Using metallic inorganic salt accelerator.

Neither of the melamine resins shows an appreciable decrease in wrinkle recovery after repeated washes when the metallic inorganic salt acclerator is used. When the melamine resins were applied with the alkanolamine hydrochloride accelerator, the MF shows excellent durability and the modified MF has only a slight loss in wrinkle recovery after repeated washes.

Although the wrinkle recovery values of the EU finish are very high initially, they generally show the greatest loss after repeated washes. As these graphs show, the EU finish loses from 40–60° in wrinkle recovery after 16 washes. The UF finish has low initial wrinkle recovery and loses about 20° in these washes.

It is doubtful if the small increases in wrinkle recovery during the last few washes shown in certain systems in Figure 22 are real since the precision of the data is less as the number of washes increases.

The durability of a finish to washing can also be measured by the resin solids remaining on the fabric. In order to compare the durability of the four resins in this manner, nitrogen determinations were made before and after 16 chlorine washings of two concentrations of UF, EU, MF, and modified MF at a cure of 4.5 min. at 320° F. using the metallic inorganic salt accelerator.

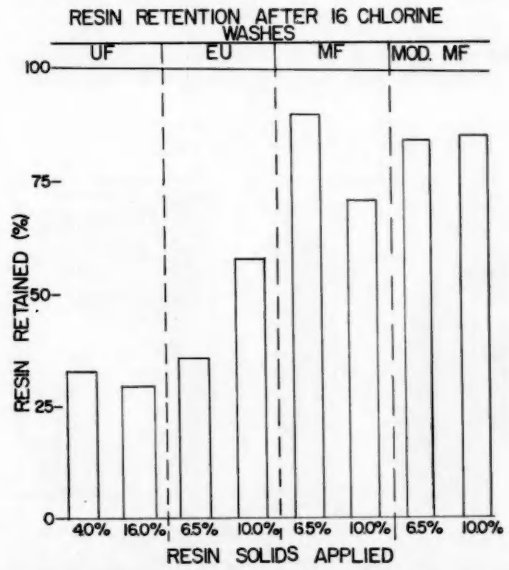

Fig. 23. Resin retention after chlorine washing.

The afterwash nitrogen values were converted to the per cent resin remaining on the fabric and plotted in Figure 23. It can be seen that the average resin retained after 16 of the chlorine-containing washings is approximately 30% for UF, 50% for EU, and 80% for MF and modified MF.

The relative durabilities of the urea and melamine formaldehyde finishes to washing in the presence of chlorine can be explained by the relative differences between the rate of acid hydrolysis of these two classes of finishes. EU and UF resins can be much more rapidly removed from cotton fabric than MF resin in water containing 1.5% of 85% phosphoric acid and 5% of urea at 85° C., as shown in Figure 24. The acid resulting from the chlorine absorbed through washing would be expected to hydrolyze similarly the UF and EU finishes much more rapidly than the MF finish.

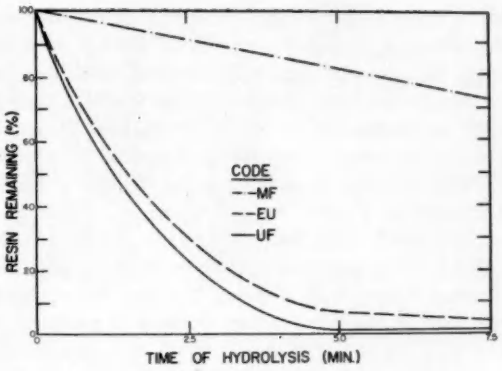

Fig. 24. Acid hydrolysis of resin finishes.

Tensile Strength

The effect of resin finishing on tensile strength has been the subject of considerable study. Figure 25 presents data showing the effect of increasing resin solids on the tensile strength. As can be seen, UF and MF finishes have higher strength than the others resins at any given solids. The EU finish has the lowest strength.

Most of the work that has been published comes to the general conclusion that as the wrinkle recovery is increased, the tensile strength is decreased.

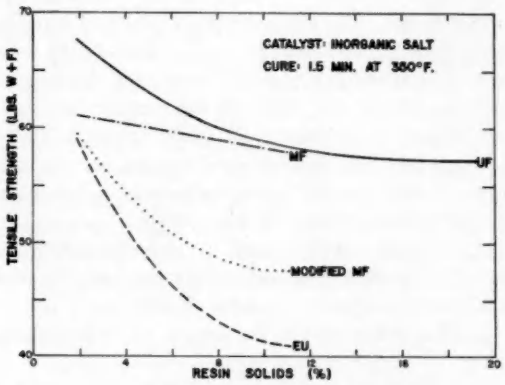

Fig. 25. Effect of resin solids on tensile strength.

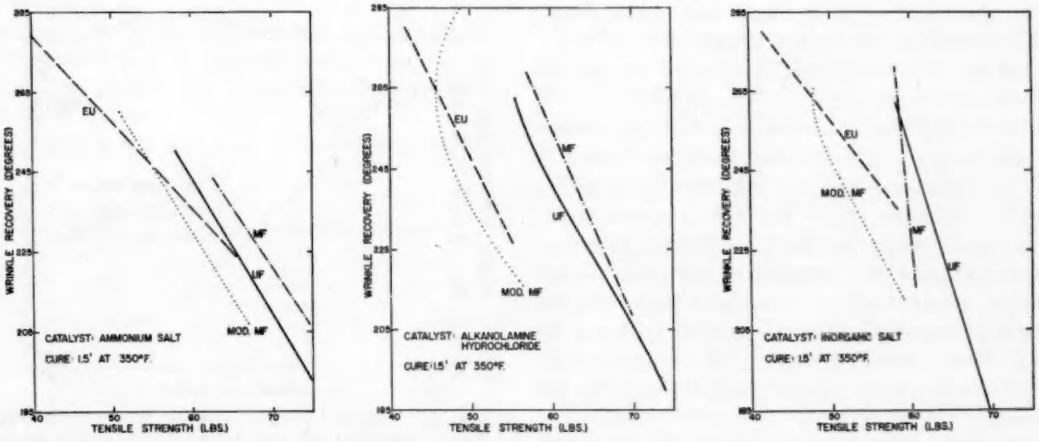

Fig. 26. Relationship of wrinkle recovery to tensile strength. *a.* Using ammonium salt accelerator. *b.* Using alkanolamine hydrochloride accelerator. *c.* Using metallic inorganic salt accelerator.

Many references state that there is a direct relationship between these two properties. Recent work by Stam [6] showed that ethylene-urea-formaldehyde finishes produce a greater loss in tensile strength than do melamine-formaldehyde finishes at equal wrinkle recovery. Our work supports this view. Plots of wrinkle recovery against tensile strength are given in Figure 26 (*a*, *b*, and *c*). The EU and modified MF finishes have a lower tensile strength than the other finishes at equal wrinkle recovery values. In general, the rate of strength loss with increasing wrinkle recovery is greater for EU than for modified MF. With the metallic inorganic salt accelerator, it is interesting to note that the graph for the MF finish shows that there is no appreciable change in strength as the wrinkle recovery increases. The strength (warp plus fill) remains fairly constant at about 58–60 lb. These data indicate, that when the tensile strength of the treated fabric is critical, the MF with the metallic inorganic salt should be considered for finishing the fabric.

There are two possible explanations for the differences in the tensile strength–wrinkle recovery relationship between the resins, namely:

1. Physical bonds caused by polymer formation within the cotton fiber rather than covalent chemical bonds across adjacent cellulose chains.

2. The difference in the length of cross-linking bonds.

If it were assumed that physical bonds permitted greater extensibility than covalent chemical bonds, the first explanation would appear to be a valid one. The authors know of no data that would justify making such an assumption, however.

On the other hand, it is conceivable that the difference in tensile strength between MF and EU finished fabric, for example, is caused by a longer cross-link of the MF compared with that of the EU. If the monomeric MF and EU directly cross-link adjacent cellulose chains, the MF cross-link would be longer than that of the EU. If with its greater functionality the MF polymerizes more than the EU before cross-linking, the length of the cross-link might be expected also to be greater than that of the EU. With a longer cross-link, greater extensibility resulting in greater tensile strength might be expected.

The effect of repeated chlorine washes on tensile strength is shown in Figure 27 (*a*, *b*, and *c*). As

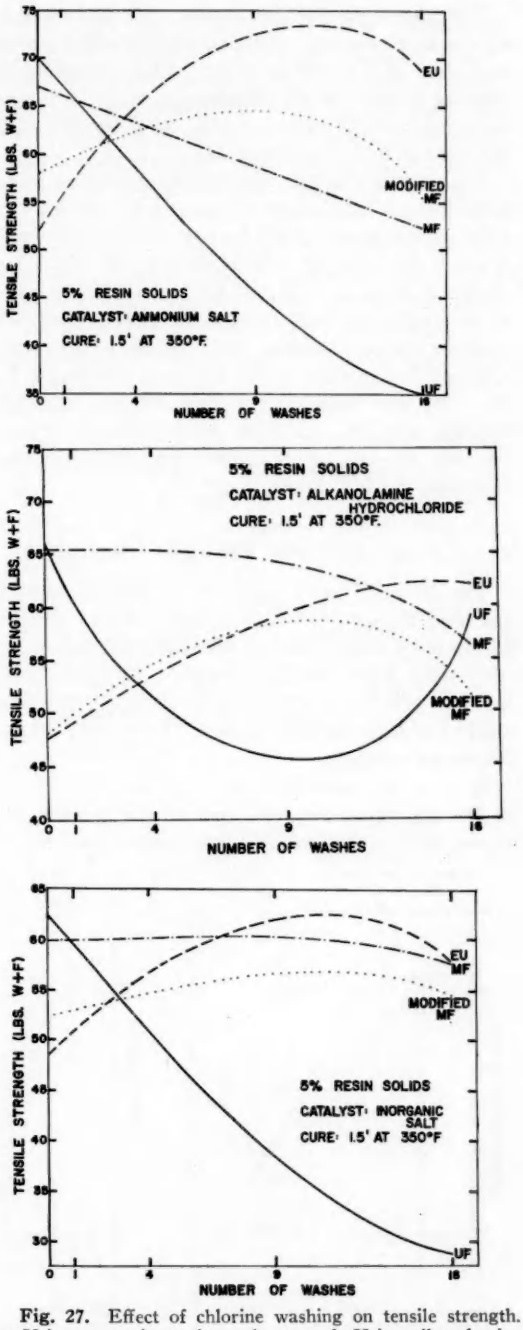

Fig. 27. Effect of chlorine washing on tensile strength. *a.* Using ammonium salt accelerator. *b.* Using alkanolamine hydrochloride accelerator. *c.* Using metallic inorganic salt accelerator.

can be seen, the UF finished fabrics generally show the greatest strength loss with repeated washes. The melamine finished fabrics in most cases show the least change in strength with repeated washings. The EU treated fabrics generally increase in strength as washing proceeds.

There seems to be an apparent inconsistency in the increase in tensile strength for the EU finish and the decrease in tensile strength for the UF finish, whereas both finishes show decreasing wrinkle recovery on repeated washes. An explanation for this apparent anomaly is that the UF has retained a considerable amount of chlorine which has caused degradation of the cotton fabric. The EU finish on the other hand did not absorb enough chlorine to degrade the fabric, but enough was absorbed to hydrolyze the cross-links with cellulose, thus recovering part of the original strength of the fabric and reducing the wrinkle recovery.

The comparatively small changes in tensile strength of the melamine resin finished fabrics on repeated chlorine washings is in keeping with their comparatively small changes in wrinkle recovery during the same washings.

The data in Table IV below show that after one chlorine wash the amount of chlorine absorbed by the EU and melamine finishes is much less than that absorbed by the UF finish.

If it is assumed that the chlorine absorbed by the resin eventually is converted into acid, the poor durability to chlorine washing of the UF and EU finishes would be expected because of their ease of acid hydrolysis. The comparatively high chlorine content of the washed UF finished fabric is in accord with the explanation that its tensile strength loss is caused by degradation of the fabric from the action of chlorine.

The bar graph in Figure 28 summarizes the influence of chlorine on tensile strength as determined by the AATCC accelerated chlorine test [7] as a function of resin, accelerator, and curing temperature. UF finished fabric does not have any appreciable resistance to chlorine as determined by this test. Fabrics treated with resins cured at 290° F. with the ammonium salt lose most of their strength under the test conditions. With other accelerators, particularly the metallic inorganic salt, at the high temperature, the melamine and EU resin treated fabrics retain most of their strength when exposed to the high chlorine concentration of this test followed by scorching.

TABLE IV. Chlorine Absorption of Resin

Resin	Solids	% Available chlorine
UF	4.2	0.4
	10.2	0.7
EU	6.5	0.1
	10.2	0.1
MF	6.5	0.1
	10.2	0.1
Modified MF	6.5	0.1
	10.2	0.1

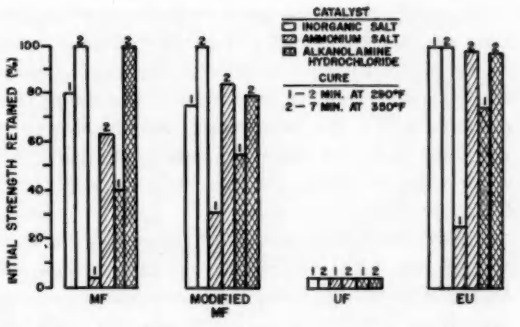

Fig. 28. Effect of AATCC accelerated chlorine retention test on tensile strength of resin finishes.

Discoloration

A fabric may discolor during resin treatment or during washing in the presence of chlorine bleach. A photometric method for quantitatively determining a yellow discoloration has been developed. This method involves measuring the per cent reflectance at 455 (R_1) and 557 (R_2) mμ and calculating the Yellowing Index by the following formula:

$$\text{Yellowing Index} = 70\left(1 - \frac{R_1}{R_2}\right)$$

A Yellowing Index value of about 3 indicates a very small degree of yellowing. In fact, the yellowing of a fabric at this value can be seen only by comparing it with a white standard. A Yellowing Index of 5 is visible with close inspection. Yellowing Index values of above 5 are easily seen.

Initial yellowing (resulting from curing—not chlorine bleaching) is affected by the time and temperature of the curing cycle.

Figure 29 shows the effect of increasing temperature on the discoloration for the different resin-accelerator systems. In general, the degree of initial yellowing tends to increase with increasing temperature. The rate of increase and the degree of yellowing is lowest when the metallic inorganic salt accelerator is used. At the higher temperatures EU generally yellows most.

Figure 30 shows the effect of curing time at 350° F. on initial yellowing. As can be seen, the degree of initial yellowing increases with increasing cure time. Here again, resins applied with the metallic inorganic salt yellow the least. EU finished fabrics yellow more than the other resin finishes when alkanolamine hydrochloride and ammonia salt accelerators are used.

Figures 31 and 32 show the discoloration due to chlorine washing (not initial yellowing) on melamine resin finished fabrics only. No data are presented for the EU or UF finishes since these do not yellow with chlorine washing.

Figure 31 shows the effect of variation of curing conditions on yellowing of MF treated fabric due to chlorine retention after 16 chlorine washes. Increasing the curing temperature or time generally decreases yellowing due to chlorine. It is significant that the use of the metallic inorganic salt results in much less yellowing due to chlorine retention than the other accelerators under the same curing conditions.

Figure 32 shows the effect of time and temperature of cure on modified MF treated fabric with regard to yellowing through 16 chlorine washings. In this case with the metallic inorganic salt the yellowing due to chlorine is hardly noticeable to the eye regardless of the temperature. There is very little yellowing with the alkanolamine hydrochloride. The yellowing with the ammonium salt acclerator is

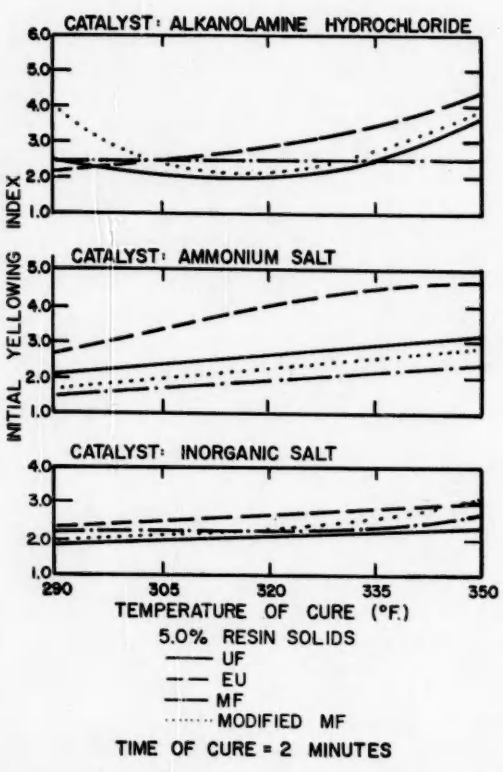

Fig. 29. Effect of curing temperature on initial color of resin finishes.

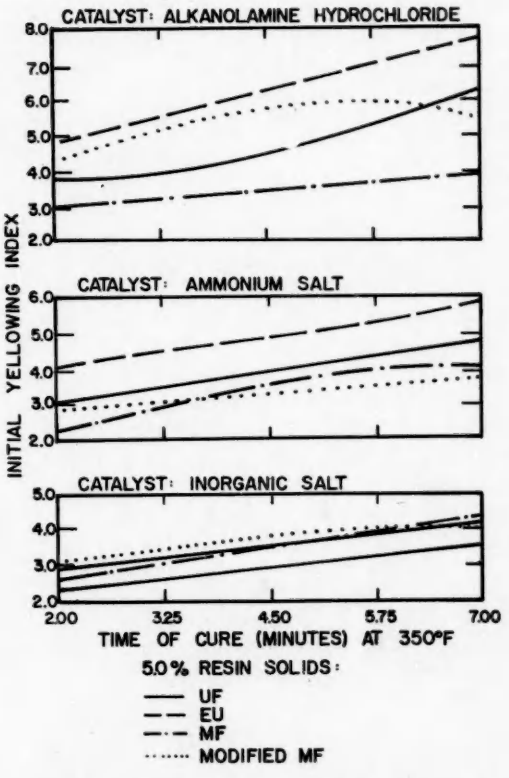

Fig. 30. Effect of curing time on initial color of resin finishes.

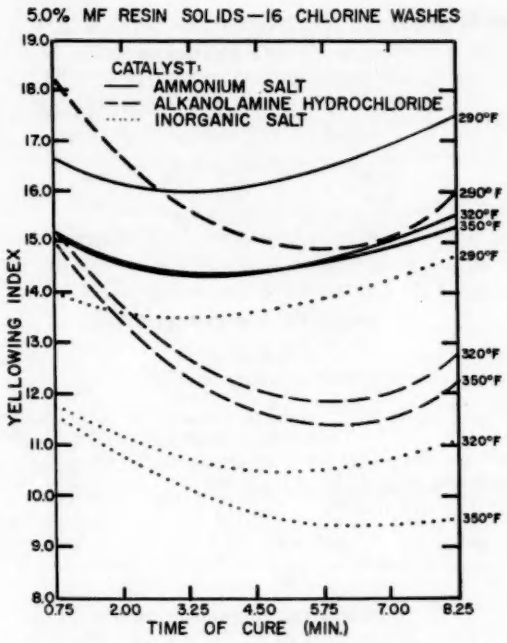

Fig. 31. Effect of chlorine washing on yellowing of melamine formaldehyde-accelerator systems.

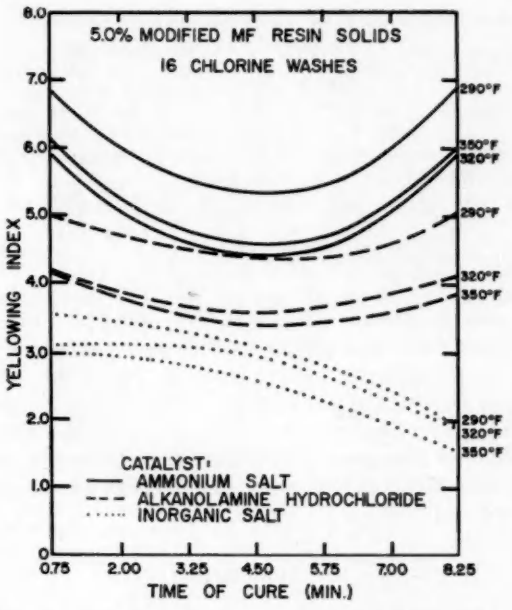

Fig. 32. Effect of chlorine washing on modified melamine formaldehyde-accelerator systems.

noticeable to the eye. It is interesting to note that the time of cure is not an important factor. In fact, with this type of resin which has very good resistance to yellowing, even the temperature of cure has little affect on the degree of yellowing.

Tear Strength

A statistical analysis of the Elmendorf tear strength values showed that there was no correlation between this property and other factors such as wrinkle recovery and resin concentration. Furthermore, the tear strength values were not reproducible. This lack of reproducibility apparently is due to the fact that the tear strength is influenced by other factors such as stiffness which varied with the application conditions. All the fabrics were, therefore, mechanically manipulated by dry tumbling to break down the stiffness and the tear strength values redetermined.

After this treatment there was a correlation between tear strength and other properties; however, there are no large differences in the wrinkle recovery and tear strength relationships for the different

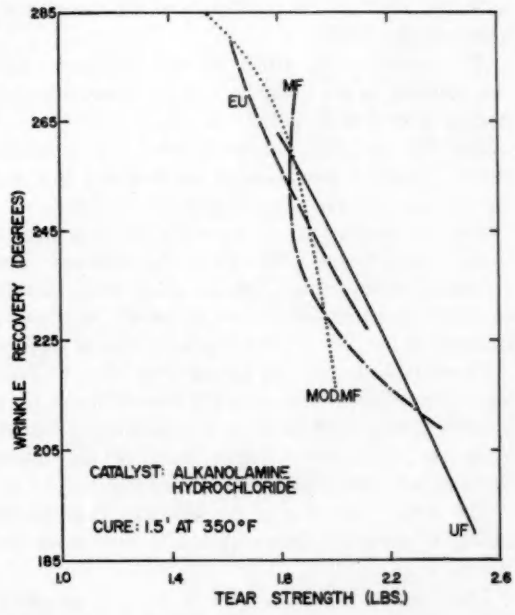

Fig. 33. Relationship of tear strength to wrinkle recovery.

TABLE V. Fabric Properties

	Wrinkle recovery		Tensile strength		
	Initial	After chlorine washing	Initial	After chlorine washing	AATCC chlorine test
Greatest ↕ Least	EU Mod. MF MF UF	MF Mod. MF UF EU	MF UF Mod. MF EU	EU MF Mod. MF UF	MF Mod. MF EU UF

systems studied. The wrinkle recovery is plotted against tear strength for the four resin finishes with the alkanolamine hydrochloride in Figure 33. As can be seen, the tear strength of the fabric decreases as the wrinkle recovery increases. All the resin finishes also show about the same relationship between these two properties with the other accelerator systems studied.

Summary

A summary of the physical properties of the finishes studied is given in Tables V and VI.

The EU finishes generally have the highest wrinkle recovery for a given resin solids, and the UF the lowest. The melamine finishes are intermediate with the modified MF equalling the EU under optimum curing conditions.

The retention of wrinkle recovery through chlorine washing of the melamine finishes is considerably greater than that of the EU or UF.

The MF and UF finishes generally have higher tensile strengths than those of the modified MF and the EU finishes for a given wrinkle recovery.

The EU finished fabric generally shows a gain in tensile strength on continued chlorine washing. The melamine resin treated fabrics show little loss in strength on continued washings, while the tensile strength of the UF treated fabric decreases rapidly.

There is little loss in strength in the AATCC accelerated chlorine test with EU and melamine resin treated fabrics that have been satisfactorily cured. With the UF treated fabric most of the fabric strength was lost under these conditions.

The initial yellowing of the treated fabric during curing is generally greater for EU than with the others.

There is no yellowing of EU or UF and very little yellowing of the modified MF treated fabric during continued washing in the presence of chlorine, but MF treated fabric does yellow.

There is little difference in tear strength for a given wrinkle recovery among the various resin finishes.

The ranking of the accelerators from best to poorest is given in Table VII.

Generally the metallic inorganic salt gives the highest wrinkle recovery, the least yellowing during curing, and the best retention of wrinkle recovery, least tensile loss and the least yellowing during chlorine washing of the accelerators studied. With this accelerator high curing temperatures are required to obtain these superior properties. The alkanolamine hydrochloride generally provides fabric properties that are inferior to those of the metallic inorganic salt accelerator but its optimum curing temperature is lower. The ammonium salt, in most cases, provides the least improvement in these fabric properties.

Although this summary gives general conclusions based on our study, it is recommended that the finisher carefully study the data contained herein

TABLE VI. Fabric Properties

	Yellowing		
	Initial	After chlorine washing	Tear strength
Greatest ↕ Least	EU MF UF Mod. MF	MF Mod. MF EU UF	EU UF Mod. MF MF

TABLE VII. Accelerator Rank

Best	Metallic inorganic salt
↕	Alkanolamine hydrochloride
Poorest	Ammonium salt

to determine the best combination of resin-accelerator and curing conditions for the particular properties that he desires in the individual fabric that he wishes to treat.

Acknowledgments

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Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

Assay of Cyanoethylated Cotton

Monsanto Chemical Company
Plastics Division
Texas City, Texas
September 10, 1956

To the Editor

TEXTILE RESEARCH JOURNAL

Dear Sir:

The reaction of cotton cellulose with acrylonitrile to yield partially cyanoethylated products has received considerable attention following recent publications of Compton and his co-workers [1, 2]. The extent of cyanoethylation is usually ascertained by determining the nitrogen content of the treated cotton. Because of its simplicity the Kjeldahl method is generally employed for these determinations.

Daul, Reinhardt, and Reid [3] have reported that the usual Kjeldahl procedure may be modified to eliminate the initial sulfuric acid digestion step. It has been learned via private communications that other workers in this field have also used the modified Kjeldahl as an acceptable analytical technique.

This practice cannot be depended on to give accurate assays of the cyanoethylated products and should not be accepted as a general method of analysis.

The data of Table I show differences obtained by the two methods in analyzing both yarns and fabrics. The last column of this table shows the magnitude of the errors which may be encountered. Duplicate analyses were made in all cases. In all cases the differences in nitrogen content between the two determinations were significantly greater than the average deviation using a given method of analysis.

Daul, *et al.* [3] state that they observed no significant differences in nitrogen assay obtained by the two methods in analysis of cyanoethylated 12/5 sewing thread. Quantitative values for the observed differences are not given, but it is entirely probable that the error in using the modified procedure was

TABLE I. Comparison of Kjeldahl and Modified Kjeldahl Procedures in Assaying Cyanoethylated Cotton

Sample	Kjeldahl, % N	Modified Kjeldahl, % N	Difference, % N	Error, %
30/2 yarn	2.73 ± 0.03	2.58 ± 0.02	0.15	5.50
30/2 yarn	3.98 ± 0.00	3.70 ± 0.00	0.28	7.04
20/2 yarn	3.87 ± 0.00	3.68 ± 0.04	0.19	4.91
3.6-oz., 80×80 print cloth	2.44 ± 0.01	2.27 ± 0.04	0.17	6.96
3.6-oz., 80×80 print cloth	3.72 ± 0.04	3.61 ± 0.01	0.11	2.96
8-oz., 74×28 duck, plain weave	4.85 ± 0.01	4.18 ± 0.02	0.67	13.8
10-oz., 74×28 duck, plain weave	2.19 ± 0.01	1.27 ± 0.05	0.92	42.0
10-oz., 74×28 duck, plain weave	4.00 ± 0.04	3.31 ± 0.01	0.72	17.8
14.9-oz. duck	3.37 ± 0.03	2.94 ± 0.02	0.43	12.8
20-oz., No. 8 duck	3.36 ± 0.01	2.92 ± 0.01	0.44	13.1

not great, especially if the thread was absorptive and easily penetrated by the caustic solution during analysis.

In analysis of the 12.9- and 20-oz. ducks, the error was about the same whether analyses were carried out on small pieces of the fabric or on yarns frayed from the fabric. This would indicate that yarn structure is a greater factor than fabric construction in determining the reliability of the modified Kjeldahl procedure.

Conditions were varied using the modified procedure in analysis of the 10-oz 4% N duck. These data are summarized in Table II. Increasing the severity of hydrolysis conditions and distillation time improved the nitrogen values obtained, but the value found by standard Kjeldahl was not duplicated by the modified technique.

TABLE II. Effect of Varying Conditions on Nitrogen Values Obtained by Modified Kjeldahl

Ml. 50% NaOH	Ml. H_2O	Distillation time, min.	% N
Standard Kjeldahl			4.00 ± 0.04
10	200	45	3.31 ± 0.01
25	200	45	3.72 ± 0.01
100	100	60	3.70 ± 0.02
25	200	90	3.81 ± 0.01

Analytical Procedure

Yarns were cut into pieces about ½ in. long; fabrics were cut into pieces about ⅜ in. square. In either case the cotton was dried overnight at 75°–80° C. and 0.3–0.4 g. samples were weighed from glass-stoppered weighing bottles.

Kjeldahl

The samples were digested in 15 ml. of concentrated sulfuric acid containing 10 g. of anhydrous sodium sulfate. Selenium metal was used as the catalyst for the digestion [5] in the form of selenium-coated boiling stones.

Digestion was continued for half an hour after the mixture became clear. The cooled digestion mixture was diluted with water, cooled, and neutralized with 50% sodium hydroxide solution to the phenolphthalein end point. The liberated ammonia and about 100 ml. of distillate were distilled into a 3% boric acid solution [4]. The ammonia was titrated with 0.1 *N* hydrochloric acid using a mixed methyl red–methylene blue indicator [6].

Modified Kjeldahl

The sample was placed in a Kjeldahl flask containing 200 ml. of water and 10 ml. of 50% sodium hydroxide solution. The water and ammonia were then distilled and collected in boric acid solution as before. Distillation was continued for about 45 min. during which time approximately 100 ml. of water were distilled over.

Conclusion

The modified Kjeldahl procedure is not generally satisfactory for the assay of cyanoethylated cotton. While it may be possible to use the modified Kjeldahl with some types of cyanoethylated cotton and obtain reliable results, this fact must be established for each type of cyanoethylated cotton before the procedure is used. No particular advantage obtains from the modified Kjeldahl. It is recommended that the standard Kjeldahl procedure be used at all times in preference to the modified procedure.

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GLEN E. JOURNEAY [1]
JOHN E. BLACKMON

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Fibrous Cellulose Esters by Trifluoroacetic Anhydride Method

Southern Regional Research Laboratory
Southern Utilization Research Branch [1]
New Orleans, Louisiana
July 2, 1956

To the Editor

TEXTILE RESEARCH JOURNAL

Dear Sir:

Because of the naturally excellent physical form of cotton, research at this laboratory in preparing cotton cellulose esters has emphasized retention of the fibrous form [2]. The "impelling" action of chloroacetic acids and their anhydrides on the esterification of cellulose by other organic acids has been described by Clarke and Malm [3], but their reaction results in the formation of soluble cellulose derivatives. The use of trifluoroacetic anhydride as an esterification "impellent" was reported by Bourne, *et al.* [1] and Tedder [5]. Only a few cellulose esters have reportedly been prepared by this method [1], and these were soluble derivatives.

We have found that the trifluoroacetic anhydride "impellent" method is generally more applicable to the partial esterification of cotton with retention of the fibrous form than a study of the literature would indicate. Furthermore, the method has certain advantages: no additional catalyst is needed, the esterifying acid is efficiently used and need not be in the anhydride form, acids with a wide variety of molecular structures may be reacted, trifluoroacetyl groups are not introduced, and the products have good textile properties. This communication reports the preparation of a wide variety of fibrous esters by the trifluoroacetic anhydride method because it is believed that the results will be of value to investigators having an interest in transformation of cotton into fibrous cellulose derivatives.

Scoured cotton yarns were reacted slack with the respective acids in the presence of trifluoroacetic anhydride with benzene as the diluent. The reaction was carried out in glass tubes closed with ground joints. The reaction tubes were tumbled end-over-end during the reaction period, usually 24 hr. at about 30° C. Upon removal from the reaction medium, the yarns were washed successively in fresh benzene, alcohol, and water. These conditions may not be optimum for all of the acids used, and the low reactivities of some of the acids would undoubtedly justify changing conditions. However, when textile properties are of interest, degrees of substitution as low as 0.02 are important.

[1] Agricultural Research Service, U.S. Department of Agriculture.

TABLE I. Partial Esters of Cotton Cellulose
(Using one equivalent of acid per anhydroglucose unit)

Acid	Acyl content, %	D.S.
Phenoxyacetic	1.4	0.02
Coumarilic	2.4	0.03
Picolinic	2.6	0.04
β-benzoylacrylic	4.3	0.05
Methoxyacetic	2.6	0.06
Phenylmercaptoacetic	9.5	0.11
Cyanoacetic	6.3	0.16
p-tert. butylbenzoic	13.4	0.16
Stearic (¼ equivalent)	23.9	0.19
β-chloropropionic	11.1	0.22
Benzoic	14.6	0.26
β-bromopropionic	19.1	0.28
Oleic (½ equivalent)	38.7	0.38
Crotonic	16.9	0.48
Sorbic	23.4	0.52
Cinnamic	32.8	0.60
n-butyric	22.7	0.66
Iso-butyric	23.9	0.71
p-methoxyphenylacetic	44.7	0.87
p-isopropylphenylacetic	46.7	0.88
Undecylenic	52.7	1.07
Cyclohexanecarboxylic	44.5	1.16
Acetic (2 equivalents)	30.6	1.64

The acyl values determined by a modified Eberstadt method [4] are listed in Table I after the names of each acid employed. The data represent single experiments, each with approximately 1 mole of esterifying acid per glucose unit present except for stearic (1/4 equivalent), oleic (1/2 equivalent), and acetic (2 equivalents).

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CARL HAMALAINEN
RICARDO H. WADE
EDMUND M. BURAS, JR.

Loom-Action-Type Abrader

The Ahmedabad Textile Industry's
Research Association
Navrangpura, Ahmedabad 9, India
September 24, 1956

To the Editor

TEXTILE RESEARCH JOURNAL

Dear Sir:

Ramirez and Vidosic have shown in a recent publition in TEXTILE RESEARCH JOURNAL that a loom-action-type abrader is superior to other types of abraders in evaluating weavability of sized yarns. They state that "such static tests as per cent elongation and tensile strength are insufficiently sensitive to sizing changes to warrant their use in assessing the weaving qualities of a sized warp" and that "if a combined stress-strain tester is to be reliable in evaluating sizing compounds, it must closely reproduce the action which a warp yarn will normally undergo in the weaving loom."

In the extensive work on sizing carried out by this laboratory in its member mills over the last five years, covering a range of warp counts from 18's to 60's, no significant correlation was found between either single-thread breaking load or extension at break of sized yarns and their warp breakage rate in large-scale weaving trials. In order to get a rapid and reliable method of comparing the large number of sizing formulations used in this work, a "dummy" loom, similar in principle to that used by Ramirez and Vidosic, and described below in detail (Figure 1) has been used in this laboratory for over three years with satisfactory results.

A sheet of 250 to 300 ends of the sized warp under test is clamped at the back of the machine, taking care to see that the yarns are parallel. These are passed through a set of healds and a reed in the same manner as in a standard loom. In evaluating a size formulation for different fabric sorts, differing in their compactness of structure, the appropriate healds and reed that would normally be used by industry, may be used also for the test, if desired. The available loom movements are shedding and reed traverse which are kept geometrically similar to actual weaving practice and take place at the same rate as in the weaving operation. The free ends of the yarns, after drawing through healds and reed, pass over a freely rotating guide roller, and after proper alignment, are fixed in another clamp. The clamp carries a pan where the required weight is kept for tensioning. The warp yarns are stationary throughout the test and therefore receive sustained flexure-abrasion. No weft yarns are inserted. The number of flexure-abrasion cycles is recorded on a revolution counter.

For routine tests, three or four different samples may be placed side by side, making available 75 to 100 ends of each sample for a test. The number of abrasion cycles required to rupture a definite fraction (usually 10%) of the sample is recorded. For each test, at least three and usually five such readings are taken and the mean computed. When more than two samples are abraded simultaneously, their relative positions are altered in successive readings, so as to avoid any bias in severity of abrasion at the ends of the reed. Figure 2 gives a set of typical data obtained on the dummy loom for six samples of yarn from the same grey stock, sized in identical manner, except that a different softener was used in each case.

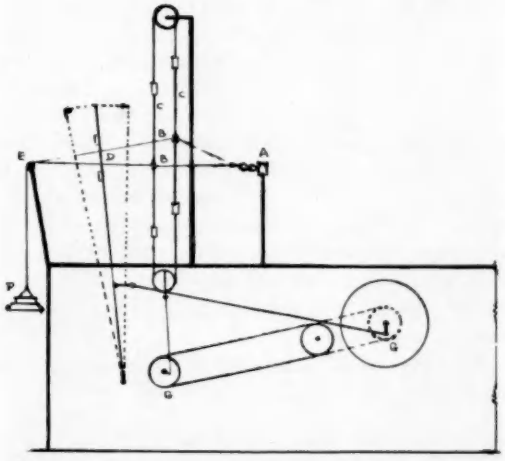

Fig. 1. Line diagram of dummy loom. A—Fixed clamp, B-B—Sheet of yarn, C—Healds, D—Reed, E—Freely rotating guide roller, F—Tensioning weights, GG—Eccentric drives.

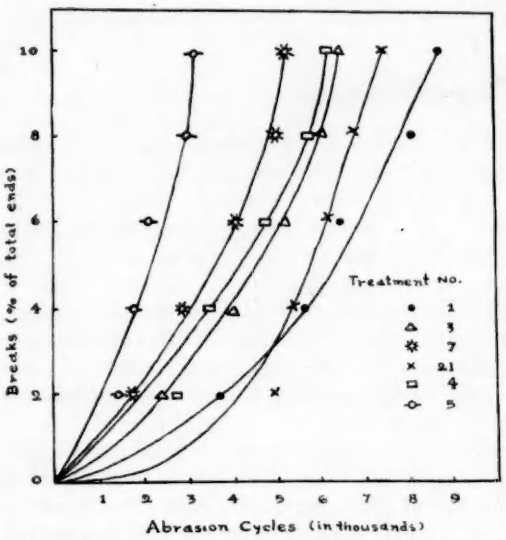

Fig. 2. Breakage rate versus abrasion on dummy loom.

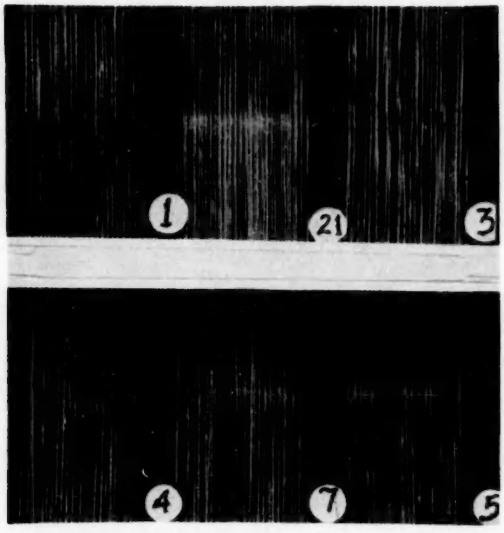

Fig. 3. Appearance of sized yarn samples after 1000 cycles on dummy loom.

One advantage of this type of loom-action abrader is that a visual examination of the yarns after abrasion also assists in the judgment of their weaving performance. Breaks originating in sizing faults are largely due to rubbing off of the size, accumulation of fluff in the reed traverse, and "balling" at the reed. Figure 3 shows the six samples referred to in Figgure 2 at the end of a test. Mere visual examination of the amount of fluff collected can help in screening out the bad from the good sizes.

Finally, data were also collected on warp breakage rate in large-scale weaving for the same six samples, along with their tensile strengths and extensions at break. Rank correlations were computed between each of these three characteristics and dummy loom data, and are given in Table I. A rank correlation coefficient of 1 was found between breakage rate on dummy loom and in large-scale weaving, while the correlation obtained with tensile strength and extension at break was not significant, proving that the dummy loom can be used with confidence to evaluate weavibility.

These results and others will be reported in greater detail at a later date.

TABLE I. Warp Breakages and Physical Characteristics of Sized Yarns

Sizing treatment no.	Breaks per 10,000 picks in large-scale weaving trials	Breaks per 10,000 abrasions on dummy loom	Mean breaking load, oz.	Mean breaking extension, %
1	1.5	5.7	9.5	3.5
3	2.7	7.8	10.1	3.6
7	3.8	9.5	10.3	4.3
21	2.2	6.7	11.0	4.9
4	3.2	9.4	9.3	5.4
5	7.2	16.1	9.3	3.0
Rank correlation against large-scale weaving trials	—	1	+0.38	+0.14

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P. C. MEHTA
C. C. SHAH

Effect of Long Storage on Cotton

ACCO Fiber and Spinning Laboratory
Anderson, Clayton & Co., Inc.
417 La Branch
Houston, Texas

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

Cotton grown in 1862 is still as strong and durable as anticipated for many samples from the 1956 crop. There is no record of these bales being tested when ginned; therefore, it is not known how much the fiber strength has decreased, but data available from other samples held in storage indicate very little change in physical properties except color. Cotton tends to yellow upon aging in storage.

The 1862 bales were grown at West Point, Mississippi, and one of them is displayed in the ACCO Fiber & Spinning Laboratory, 417 La Branch, Houston, Texas; the other one is on the floor of the New Orleans Cotton Exchange in New Orleans, Louisiana. The fiber strength of the ACCO bale is essentially equal to that of the average Strict Middling 15/16-in. staple cotton grown in the United States during the past three crop years (Table I). The Micronaire reading was higher than the average of recent growths, as was the upper half mean length. The yarns spun from the ACCO bale were stronger, the nep count was lower, and the yarn appearance grades were superior to the average of the cottons ginned in the past three crop years.

These data demonstrate that there is no appreciable deterioration of raw cotton, as long as it is undamaged when stored and the storage conditions are dry. In humid, hot climates, cotton will tend to yellow upon aging. Little or no loss in strength is expected, however, unless the moisture in the cotton exceeds 9%, based on the dry weight of the cotton.

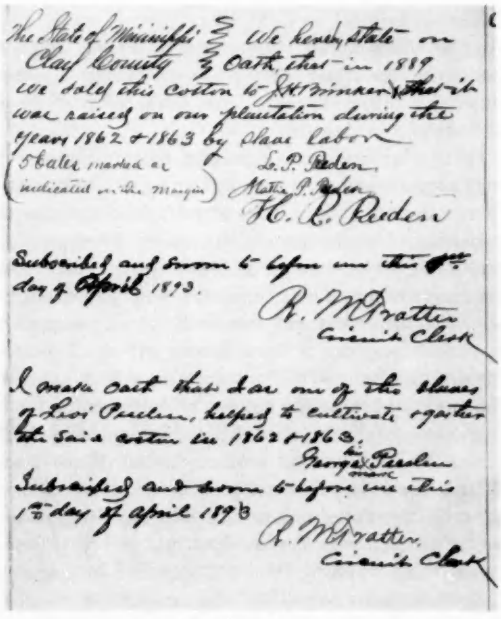
The State of Mississippi } We Lewis Pearlen on
Clay County } oath that in 1889
we sold this cotton to J.H. Minnan & that it
was raised on our plantation during the
years 1862 & 1863 by slave labor
5 bales marked as Le. P. Pearlen
indicated on the Margin Martha P. Pearlen
H. L. Pearlen
Subscribed and sworn to before me this 9th
day of April 1893.
R. McGratten
Circuit Clerk
I make oath that I am one of the slaves
of Levi Pearlen, helped to cultivate & gather
the said cotton in 1862 & 1863.
his
George X Pearlen
mark
Subscribed and sworn to before me this
10th day of April 1893
R. McGratten
Circuit Clerk

Fig. 1. Affidavit confirming origin and sale of bales of cotton harvested and ginned in 1862.

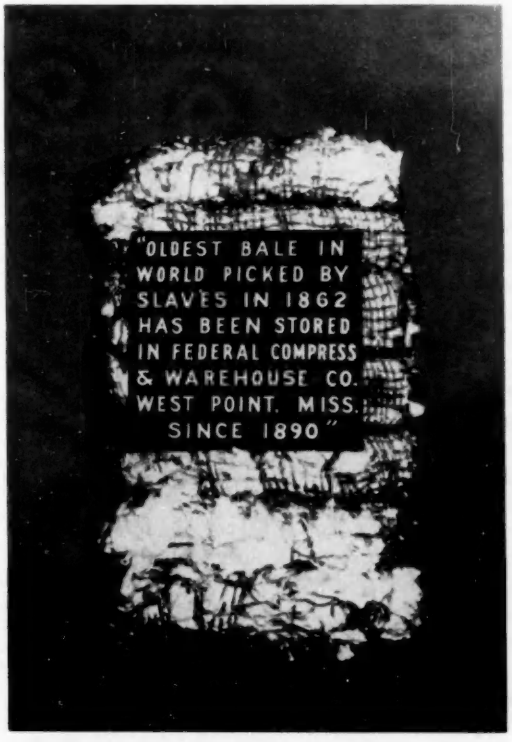

Fig. 2. Bale of 1862 cotton as received by Anderson, Clayton & Co.

TABLE I. Fiber and Spinning Data on Bales of Cotton Ginned in 1862 Compared with the Average Fiber and Spinning Data on Strict Middling Grade and Better 15/16 in. Staple Cottons Tested in the ACCO Laboratory for the Years of 1953, 1954, and 1955

	Cotton grown in 1862			
	Bale No. 1 ACCO lab, Houston, Texas	Bale No. 2 New Orleans Cotton Exchange	Average from bales in current production*	Current production, hand picked and ginned on laboratory gin
Classer's grade	SM Lt. Sp.	SM Sp.	SM & SM Lt. Sp.	SLM Lt. Sp.
Classer's staple length	15/16"	15/16"	15/16"	15/16"
Fibrograph				
UHM length (in.)	0.96	0.93	0.94	0.95
Pressley				
Strength, 1000 lb./sq. in.	81	76	82	82
Micronaire, fineness	5.3	5.1	5.1	4.5
Waste				
Nonlint content, %	2.7	—	3.3	3.5
Picker and card, %	7.6	—	7.9	9.4
Card web appearance				
Neps per grain	3.2	2.5	7.2	16.2
Neps per 100 sq. in.	9	7	20	45
Trash per 100 sq. in.	5	3	4	18
Seedcoat fragments	5	—	—	—
Yarn skein strength, lb.				
22's	108.1	91.2	100.5	116.1
Number-strength product	2380	2010	2114	2560
Yarn appearance grade				
22's	A−	A−	B−	B+
Index	120	120	105	117

* Data represent 43 bales, all Strict Middling 15/16 in. cotton, tested in the ACCO laboratory, from the 1953, 1954, and 1955 crops. Texas to Georgia and Carolina growths.

The major differences in yarn appearance grades between the old and new cottons can, no doubt, be accounted for by the differences in methods used in harvesting and ginning the cotton. The 1862 bales were hand picked and supposedly ginned on a small hand gin by slave labor. An affidavit concerning the origin of the bales is shown in Figure 1. Bale No. 1, as received by Anderson, Clayton & Co., is shown in Figure 2. The bagging was so weak and had been cut at so many places by souvenir hunters that it was necessary to replace it. The bale is now housed in a dust-proof plastic case in the ACCO laboratory.

Current cottons, when harvested and ginned carefully at the correct moisture content and without excess machining, will also produce high-grade yarns, as shown in Table I. The Strict Low Middling cotton, the data of which are in column four of Table I, was hand picked and ginned on a laboratory gin. Although the classer's grade was Strict Low Middling, the yarn strength and appearance grade were higher than the average of those for Strict Middling cotton from the past three crops. Present-day medium to short staple cottons are, therefore, of good quality, but harvesting and ginning procedures necessitated by labor shortages are harsher than those used several decades ago.

These fiber and yarn data and the appearance of small pieces of fabric woven in the ACCO laboratory from both of the 1862 bales attest to the stability of American Upland-type cottons under good storage conditions. The data in Table I also indicate that current growths, when harvested and ginned carefully, will produce yarns essentially equal in appearance to those from cottons grown in earlier years. These data confirm the opinions of expert classers who examined these old cottons and designated them of good to excellent character. Similar bales held in storage for 30 to 60 years by estates have been designated to be of excellent character by cotton classers; therefore, creamy cottons resulting from storage are not to be confused with tinged or yellow-stained bales resulting from cotton killed by a freeze or spotted bales resulting from insect or disease damage.

EARL E. BERKLEY

The Effect of Chemical Modification on the Flame and Glow Resistance of Cotton Cellulose

Textile Research Institute
Princeton, New Jersey
September 30, 1956

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

A new series of chemically modified cotton celluloses has been prepared. These new chemical derivatives of cotton appear to have good flame and glow resistance.

Fundamental studies on the pyrolytic degradation of cellulose and cellulose derivatives carried out in this laboratory furnished the data to support a theory of cellulose decomposition at elevated temperatures [7]. This theory suggests the proximal cause of the flammability of the cellulose polymer to be the decomposition during thermal degradation of an intermediate product, 1,6-anhydro-β-D-glucopyranose (levoglucosan), to yield volatile and flammable products. This research gave rise to the working hypothesis that suitable chemical modification of the primary alcohol group at the 6 carbon of the glucose anhydride unit of the cellulose chain should prevent the formation of levoglucosan in those glucose residues so modified, and result in decreased flammability and improved glow resistance [5]. Introduction of the appropriate group should also facilitate the subsequent introduction into the cellulose molecule of certain known flame-retardant elements, such as the halogens, via a replacement mechanism [6].

Accordingly the chemical modification of cellulose in the form of cotton fabrics has been accomplished. This has been done by the esterification of the 6-OH group with sulfonyl halide, followed by partial replacement of the sulfonyloxy groups with halogen. A method of phosphorylation has also been developed and used on these same fabrics separately and in combination with the afore-mentioned modification procedure.

Helferich and Gnüchtel [2] esterified glucose derivatives in a homogeneous system with methanesulfonyl (mesyl) chloride in pyridine solution. This reaction was applied to cotton linters by Wolfrom, *et al.* [9] in 1941, and according to an unpublished report, some work on the mesylation of cotton fabrics has recently been done by the Southern Utilization Research Branch, Agricultural Research Service, U.S.D.A., New Orleans, Louisiana. The analogous reaction of tosylation is better known and was described for glucose derivatives by Oldham and Rutherford [4]. In both cases a high degree of selectivity for reaction with the 6-OH group was noted. Several workers have reported replacement of the sulfonate ion in such derivatives with iodide [1, 2, 3], and replacement with fluoride has also been recorded [3] in homogeneous reactions employing organic solvents.

Both 6-oz. cotton cloth and 9-oz. sateen were successfully mesylated in a heterogeneous reaction in pyridine after pretreatment with alkali to facilitate the main reaction. The resultant mesyl cellulose showed moderate flame and glow resistance, but failed the match test described by Reid, *et al.* [8].

The effect of partially replacing the mesyloxy ($-OSO_2CH_3$) groups with halogens was then studied. Iodine was readily introduced, using methods described for mesyl glucose derivatives and mesyl cellulose acetates [2, 9]. It was deemed highly desirable to prepare the bromo modification in view of the proved value of this element as a flame-retardant agent. However, no method appeared to have been reported in the literature for the introduction of bromine. Therefore a suitable method was developed which permitted the preparation of partially substituted iodo-, bromo-, chloro-, and fluoro-derivatives of mesyl cellulose. This method overcame the stumbling block of the relative insolubility of the halogen salts (excepting the iodide) in organic solvents, hitherto thought to be necessary for the reaction, by using an aqueous solution of the desired alkali halide. Thus bromine and the other halogens were introduced into the cellulose molecule. It was found that the pH of the reaction mixture had to be carefully controlled to avoid acid degradation of the fabric under treatment. The reaction is shown below.

$$R_{cell} - OSO_2CH_3 + NaX$$
$$+ \text{aq.} \xrightarrow{pH \cong 7} R_{cell} - X + CH_3SO_3Na$$

In the above reaction X equals I, Br, Cl, or F.

The complete series of these mesyl halocelluloses was prepared. The match test was used as a criterion for flame resistance. The mesyl iodocellulose and the mesyl bromocellulose exhibited good flame resistance in both the lightweight and the heavier weight fabrics. The mesyl chlorocellulose was comparable to mesyl cellulose, failing the match test. The mesyl fluorocellulose modification showed the poorest flame resistance.

Preliminary data on these modifications indicate that good flame resistance can be attained with a relatively low increase in fabric weight. Some data are shown in Table I.

TABLE I. Match Test Results on Modified 6-oz. Cotton Cloth

Modification	Per cent wt. increase	Char length (in.)
Mesyl bromo-	7	5.3
" iodo-	11	1.8
" bromo-	12	2.5
" iodo-	15	2.0
" bromo-	22	3.3
" iodo-	24	1.8
" iodo-	31	1.8

The glow resistance of the mesyl halocellulose is not always satisfactory, especially at the minimum treatment level. To correct this deficiency, methods by which phosphorus, well-known as a glow-retardant agent, could be introduced were investigated. The methods extant for the phosphorylation of cellulose appeared to have serious disadvantages, such as (1) severe fabric tenderization, (2) alkali sensitivity of the derivatives, and (3) lack of durability to laundering. A method in which these disadvantages could be largely overcome was therefore devised. An organo-halophosphate, diethyl chlorophosphate, was used in pyridine medium in a reaction analogous to mesylation. A phosphorylated cotton was thereby produced that had suffered little or no significant tenderization and was characterized by a complete and indestructible glow resistance. Using this method, any weight cotton fabric can be phosphorylated without pretreatment to give a derivative that exhibits moderate flame resistance (i.e., will not pass the more rigorous match test and ASTM Vertical Flame Test) but excellent glow resistance, with a fabric weight increase of as low as 4 to 5%.

A combination of phosphorylation and mesylation followed by halogen replacement was found effective in producing chemically modified cottons having good flame and glow resistance, which are theoretically permanent properties.

Some data on these combination modifications, mesyl phosphohalocelluloses, are shown in the following tables:

TABLE II. Match Test Results on Modified Cottons

Weight cotton (oz.)	Modification	Per cent wt. increase	Char length (in.)	After-glow
6	Mesyl phosphobromo-	15	3.2*	0
6	" " "	20	2.8	0
9	" " "	15	2.2	0
9	" " "	12	3.2†	0
6	" " iodo-	17	2.2	0

* Two samples out of five burned entire length.
† One sample out of seven burned entire length.

TABLE III. Results of a Single ASTM Vertical Flame Test on Modified Cottons

Weight cotton (oz.)	Modification	Per cent wt. increase	Char length (in.)	After-flame (sec.)	After-glow (sec.)
6	Mesyl phosphobromo-	14	4.9	0	0
6	" " iodo-	17	5.2	0	0
9	" " bromo-	15	4.6	0	0

A thorough study of the mechanical properties of these new textile materials has not yet been accomplished, but preliminary physical testing indicates no loss of breaking strength as a result of mesylation and halogen replacement. Preliminary experiments also indicate the flame- and glow-resistant properties of the modified cottons to be stable to laundering.

The details of this work will be published subsequently in a series of papers dealing with the pyrolytic decomposition of cellulose and cellulose derivatives, methods of chemically modifying cellulose, and the effects of chemical modifications on the flame and glow resistance of cotton cellulose.

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opment Command, Quartermaster Research and Development Center, Natick, Massachusetts.

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EUGENE PACSU
ROBERT F. SCHWENKER, JR.

Effect of Heat and Ginning Operations on Spinning and Weaving[1]

Joanna Cotton Mills Co.
Joanna, S. C.
Oct. 11, 1956

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

Joanna Mills has recently completed a test on the effect of heat and ginning operations on spinning and weaving. The test was sponsored and supervised by the Institute of Textile Technology with the full cooperation of the participating ginners and gin manufacturers. This particular test differs from previous tests in being specific as to the degree of heat applied at the gin passage and also the type of lint cleaners used following the gin. As in previous tests, it was established beyond reasonable doubt that high gin heat is detrimental to the cotton fibers.

Under the supervision of ITT technologists, lots

[1] Presented at a meeting of the Technical Quality Control Association, Greensboro, N.C., September 28, 1956.

TABLE I. Effect of Gin Temperatures on Mill Processing. Test Data from Various Gin Set-Ups

	Murray Saw		Shirley unit and Lummus Super Jet		No Lint Cleaners		Lummus Super Jet	
	High heat	Low heat	High heat	Low heat	High heat	Low heat	High heat	Low heat
	Lot 1	Lot 5	Lot 2	Lot 8	Lot 3	Lot 6	Lot 4	Lot 7
% Waste opening	0.25	0.34	0.15	0.39	0.42	0.38	0.30	0.45
% Waste picking	0.68	0.55	0.29	0.43	0.81	0.78	0.45	0.84
% Waste cards	4.37	4.32	4.34	4.16	4.79	4.64	4.34	4.94
% Total	5.30	5.21	4.78	4.98	6.02	5.80	5.09	6.23
Card neps	59	50	102	84	44	50	40	45
Filling yarn No.	38.2	37.4	39.4	38.0	39.0	37.9	38.4	37
Skein break. filling corrected to 40.0	48.71	50.48	43.02	45.47	47.72	51.45	49.05	51.56
Filling break. factor	2071	2183	1829	1887	1974	2147	2081	2186
Filling end breakage	37.91	26.07	155.6	59.95	53.45	37.52	39.92	41.14
Warp yarn No.	30.27	30.24	31.07	30.88	30.45	30.12	29.96	30.51
Warp yarn break	77.1	78.5	68.0	72.7	76.7	79.6	79.1	81.2
Warp break. factor	2334	2374	2113	2245	2336	2398	2370	2477
Warp end breakage	34.41	31.19	93.63	80.36	38.20	40.28	42.05	42.96
Loom stoppage	0.860	0.540	1.044	0.683	0.610	0.614	0.786	0.734

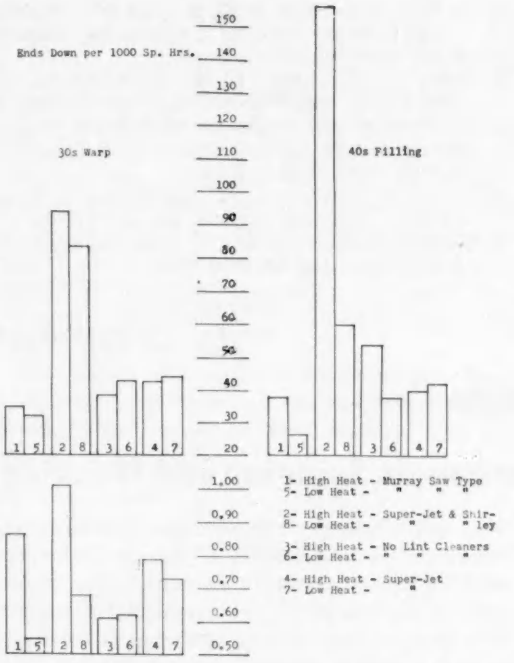

Fig. 1. Effect of gin temperatures with various gin set-ups on spinning and weaving.

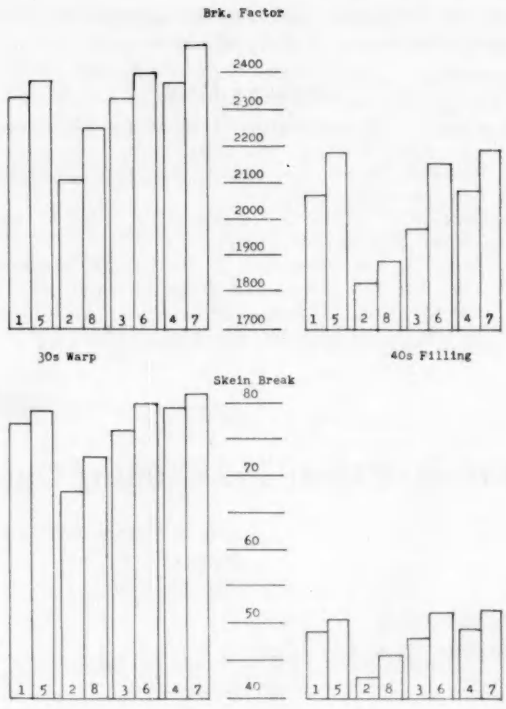

Fig. 2. Effect of gin temperatures on break factors.

of cotton were picked out with the idea of getting each as similar as possible to each other in all ways. Eight different lots of five bales each, were set up and processed at the gins as follows.

Lot 1. Murray Saw-Type Lint Cleaner, high heat in 340°, out 215° F.

Lot 2. Lummus Super Jet Lint Cleaner and Shirley Unit, high heat 340°–215° F.

Lot 3. No Lint Cleaners, high heat 340°–215° F.

Lot 4. Lummus Super Jet Cleaners, high heat 340°–215° F.

Lot 5. Murray Saw-Type Lint Cleaner, low heat in 160°, out 145° F.

Lot 6. No Lint Cleaners, low heat 160–° 145° F.

Lot 7. Lummus Super Jet Cleaners, low heat 160°–145° F.

Lot 8. Lummus Super Jet Cleaners and Shirley Unit, low heat 160°–145° F.

As can readily be seen, we have three-type gin set-ups plus the fourth with no cleaners at all. Each of these set-ups ginned cotton at both high and low heat. These bales were shipped to Joanna, and under the supervision of ITT engineers, were processed in our regular manner. All the stock was passed through the same machines to reduce any chance of machine variation.

Wastes made in the opening, picking, and carding operations were very carefully collected and weighed in order to find the per cent of waste loss. After each lot was run, the machines were thoroughly cleaned and no pains were spared to ensure the validity of this test either by ITT or by the Joanna laboratory staff, who did the actual work. Table I and Figures 1 and 2 summarize the test results.

J. L. DELANY